Recent Advances in Synthesis and Properties of Nitrated-Pyrazoles Based Energetic Compounds

Shijie Zhang 1,†, Zhengu Gao 1,†, Di Lan 1, Qian Jia 1, Ning Liu 2,*, Jiaoqiang Zhang 1,† and Kaichang Kou 1,†

1 MOE Key Laboratory of Material Physics and Chemistry under Extraordinary, School of Chemistry and Chemical Engineering, Northwestern Polytechnical University, Xi’an 710072, China; zsj562389@sina.com (S.Z.); gaozhenguo@mail.nwpu.edu.cn (Z.G.); landi@mail.nwpu.edu.cn (D.L.); qqianjia@163.com (Q.J.)

2 Xi’an Modern Chemistry Institute, Xi’an 710065, China; flackliu@sina.com

* Correspondence: zhangjq@nwpu.edu.cn (J.Z.); koukc@nwpu.edu.cn (K.K.)

† These authors equally contributed to the work.

Abstract: Nitrated-pyrazole-based energetic compounds have attracted wide publicity in the field of energetic materials (EMs) due to their high heat of formation, high density, tailored thermal stability, and detonation performance. Many nitrated-pyrazole-based energetic compounds have been developed to meet the increasing demands of high power, low sensitivity, and eco-friendly environment, and they have good applications in explosives, propellants, and pyrotechnics. Continuous and growing efforts have been committed to promote the rapid development of nitrated-pyrazole-based EMs in the last decade, especially through large amounts of Chinese research. Some of the ultimate aims of nitrated-pyrazole-based materials are to develop potential candidates of castable explosives, explore novel insensitive high energy materials, search for low cost synthesis strategies, high efficiency, and green environmental protection, and further widen the applications of EMs. This review article aims to present the recent processes in the synthesis and physical and explosive performances of the nitrated-pyrazole-based Em, including monopyrazoles with nitro, bispyrazoles with nitro, nitropyrazolo[4,3-c]pyrazoles, and their derivatives, and to comb the development trend of these compounds. This review intends to prompt fresh concepts for designing prominent high-performance nitropyrazole-based EMs.

Keywords: nitrated pyrazoles-based; energetic salts; synthesis; high energy density material; insensitivity

1. Introduction

Energetic materials (EMs), including explosives, propellants, and pyrotechnics, are a significant class of compounds containing large amounts of stored chemical energy, which can liberate heat and exert high pressure under some stimuli, like impact, shock, or thermal effect [1–8]. With the development of science and technology, more and more attention has been paid to the high energy density materials (HEDMs) used for energy and as explosives or propellants [9]. Thus, the representatives of traditional HEDMs are 2,4,6-trinitrotoluene (TNT) [10,11], 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) [12,13], 1,3,5-trinitro-1,3,5-triazine (RDX) [14], triminitrotrinitrobenzene (TATB) [15], and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaaazaisowurtzitane (CL-20) [16]. The key properties for HEDMs include density (ρ), melting point (Tm), decomposition temperature (Td), heat of formation (HOF), calculated detonation velocity (D), calculated propagation velocity of detonation wave in explosive grain), calculated detonation pressure (P, calculated pressure on the front of detonation wave), oxygen balance (OB,
residual amount of oxygen when explosive explodes to produce CO₂ and H₂O, OB = 16[c-(2a + b/2)]/M for molecule C₄H₆O₃N₄], specific impulse (Iₚₑₜ, impulse produced by the unit quantity of propellant), content of nitrogen (N), impact sensitivity (IS, sensitivity of explosive to impact), friction sensitivity (FS, sensitivity of explosive to friction), electrostatic discharge sensitivity (ESD), and sensitivity of explosive to electrostatic discharge, etc. There are several standards a novel HEDM should meet if it would be applied widely, including insensitivity toward mechanical stimuli (heat, impact, fraction, and electrostatic discharge) to ensure the safety of operation, high performance for various purposes, less toxicity, and producing less hazardous waste after detonation [17–19]. Among them, conflict between the increasing energetic level and decreasing sensitivity has become more and more severe. Therefore, the exploration and development of high energy density compounds with low sensitivity have been a priority. A significant amount of effort has been made to resolve this problem, such as recrystallization of Ems [20], preparing polymer bonded explosives (PBXs) [21,22], forming energetic cocrystals [23–25], and synthesizing novel energetic compounds [26–29]. In contrast with other technologies, synthesizing new HEDMs may be the most direct and effective method.

Nitrogen heterocyclic energetic materials that have large numbers of N–N bonds and C–N bonds with high energy can form the large π bond similar to benzene, which endows this kind of compounds low sensitivity, high positive heat of formation, and good thermal stability. In addition, the low percentage of C and N in these compounds always lead to high density and good oxygen balance. The decomposition of these compounds can result in the N₂, which is environmentally friendly [30]. There is a big difference between nitrogen-rich energetic compounds and traditional explosives, namely the energy of nitrogen heterocyclic compounds is released from the high positive heat of formation rather than the oxidation of carbon backbone like traditional explosive (such as TNT and TATB) [19,31]. Therefore, nitrogen heterocyclic materials have garnered large interest in the research areas of HEDMs.

As an outstanding representative of nitrogen heterocyclic compounds, nitropyrazoles and their derivatives are aromatic stable substances with π electrons in their structures. The system is easy to carry out electrophilic substitution reactions such as nitration, sulfonation and halogenation, etc. [32]. These compounds are characterized by oxidation resistance, heat resistance and hydrolysis resistance [19], and are widely applied in civil fields, such as medicine, pesticide, photosensitive materials, and fine chemicals [33–35]. Due to the compactness, stability, and modifiability of the molecular structure of pyrazoles, nitration and derivatization of pyrazoles are relatively easy. The ring tension in the structures of nitropyrazoles and their derivatives is large. The density and nitrogen content of nitropyrazoles increase with the presence of nitro groups on the ring, and the oxygen balance is closer to the ideal value, which can improve the detonation performance of the target compounds. Many energetic compounds based on nitropyrazoles have been synthesized successively, which have good applications in highly energy insensitive explosives, propellants, pyrotechnic agents, and other fields [2,3,19,36,37].

In the past decade, a lot of papers on the synthesis and properties of nitrated pyrazoles have been published, including many Chinese references which are not accessible for most Western researchers due to language barriers. This review article presents the recent processes in synthesis, physical and explosive performances of the nitropyrazole-based Ems, including monopyrazoles with nitro, bispyrazoles with nitro, nitropyrazolopyrazoles and their derivatives, and to comb the development trend of these compounds. The aim of this review is to provide readers with an overview of the relationship between structures and properties and guide the future design of novel HEDMs. This review also intends to prompt fresh concepts for designing prominent high-performances nitropyrazole-based EMs.

2. Nitrated-Monopyrazole Based Compounds

In this section, the sum of nitro group substituted on carbon position of pyrazole ring in mononitropyrazoles, binitropyrazoles, and trinitropyrazoles are one, two, and three, respectively.
For example, mononitropyrazole represents that only one C position in pyrazole ring is substituted by the nitro group.

2.1. Mononitropyrazoles and Their Derivatives

Mononitropyrazoles and their derivatives due to their energetic property are favored by people in many fields, such as medicine, pesticide, energetic material and so on. Among them, 3-nitropyrazole (3-NP), 4-nitropyrazole (4-NP), 1-methyl-3-nitropyrazole (3-MNP), and 1-methyl-4-nitropyrazole (4MNP) are typical examples, which are commonly used as energetic materials and intermediates for further products of other energetic materials because they contain only one nitro group and have relatively low energy. The syntheses of these compounds is often facile and can meet the development requirements of green chemistry.

As a typical heterocyclic compound, 3-NP is an important intermediate in the synthesis of pyrazole-based compounds such as 3,4-dinitropyrazole (DNP) and other new explosives [36,38]. In 1970, Habraken and co-authors [39] firstly reported synthesis of 3-NP by dissolving N-nitropyrazole in anisole for 10 h at 145 °C. Later, Verbruggen et al. [40] synthesized 3-NP from diazomethane and chloronitroethylene by one-step cyclization, while this reaction was high riskful due to the extremely vivacious raw materials. Nowadays, the main synthesis method of 3-NP was a two-step reaction, that is, nitration of pyrazole to obtain N-nitropyrazole and then rearrangement of N-nitropyrazole in organic solvent to acquire 3-NP (Figure 1, Scheme A). The nitration agents could be HNO$_3$/H$_2$SO$_4$ or HNO$_3$/Ac$_2$O/HAc, and the organic solvent for rearrangement could be anisole, n-octanol and benzonitrile [41–43]. Among these solvents, benzonitrile was always preferred to be the rearrangement medium since anisole could require an excessively long time and n-octanol would lead to poor-quality product. In 2014, Zhao et al. [44] reported one convenient and green approach to synthesizing the 3-NP. They chose the oxone as the nitration agents of 3-aminopyrazole and water as the solvent (Figure 1, Scheme B). This approach owns some advantages over the previous approach: simple operation, safety, economical reagents, the use of water as solvent, and mild conditions. As shown in Figure 1, 3-MNP is one of the most important derivatives of 3-NP. Its synthesis is mainly accomplished by nitrated 1-methylpyrazole with various nitration agents. Katritzky et al. [45] added 1-methylpyrazole to trifluoroacetic anhydride for 1 h in ice bath, and then concentrated nitric acid was added in the solution. After stirring for 12 h, and evaporation of trifluoroacetic anhydride and nitric acid, the 3-MNP could be obtained (Figure 1, Scheme C). In 2013, Ravi et al. [46] proposed that 1-methylpyrazole could reacted with silicon oxide-bismuth nitrate or silicon dioxide-sulfuric acid-bismuth nitrate in tetrahydrofuran (THF) to produce 3-MNP (Figure 1, Scheme D), this facile route is a synthetic method of low toxicity, high efficiency, and green environmental protection. In addition, metal salts of 3-NP expand its derivatives. Li et al. [42] prepared the metal Cu(II) salt and basic Pb salt of 3-NP, by dissolving 3-NP in NaOH solution and reacting with the CuSO$_4$·5H$_2$O solution and Pb(NO$_3$)$_2$ solution, respectively (Figure 1, Scheme E).

4-NP is an isomer of 3-NP with melting point of 163–165 °C, density of 1.52 g/cm$^3$, detonation velocity of 6.68 km/s and detonation pressure of 18.81 Gpa [47]. Similar to 3-NP, 4-NP can be obtained by nitro group rearrangement. As Rao et al. [48] reported N-nitropyrazole could be rearranged to 4-NP in sulfuric acid at room temperature (Figure 2, Scheme A). Ravi et al. [49] synthesized 4-NP in THF with 4-iodopyrazole as raw material, fuming HNO$_3$ as nitration agents, octahedral zeolite or silica as solid catalyst (Figure 2, Scheme B). Li et al. [50] reported one-pot two steps route that pyrazole could be nitrated to 4-NP by fuming HNO$_3$ (90%)/fuming H$_2$SO$_4$ (20%) (Figure 2, Scheme C). 4-MNP is another important derivative of nitropyrazole with the similar performance to 3-MNP (Table 1). In 2015, Corte et al. [51] reported that 4-MNP could be synthesized by adding sodium hydride and iodomethane into the THF solution of 4-NP at room temperature for overnight. Ioannidis et al. [52] improved the method by adding sodium hydride and iodomethane to the acetonitrile solution of 4-NP under nitrogen protection for 16 h. However, it is dangerous to handle sodium hydride due to its high chemical reaction activity which can easily cause combustion and explosion, limiting the further application of
this method. Han et al. [53] simplified the above method and replaced sodium hydride with potassium carbonate. They added potassium carbonate and iodomethane to the 4-NP in dimethylformamide (DMF) solution at 25 °C for 14 h. This method not only reduces the risk in the process, but improves the reaction yield (80–98%).

**Figure 1.** Summary of synthesis of 3-NP, 3-MNP and metal salts of 3-NP.

![Figure 1](image1.png)

**Figure 2.** Synthesis of 4-NP.

![Figure 2](image2.png)

Table 1 shows the energetic performances of the four typical monopyrazoles. We can see that these energetic performances of pyrazole-based compounds are not satisfying, especially the detonation properties and the nitrogen content. So, these nitropyrazoles are always used as intermediates for the preparation of novel high-performance energetic materials. Furthermore, it is also necessary to explore new high performances energetic materials based on mononitropyrazoles. For example, Deng et al. [54] prepared 5-methyl-4-nitro-1H-pyrazol-3(2H)-one (MNPO) and its energetic salts, showing better performances than these above mononitropyrazoles.
The introduction of a polynitromethyl group into a heterocyclic compound is interesting for energetic field, because it can increase the oxygen content and improve the energetic properties of energetic material. Generally, the incorporation of a polynitromethyl group (trinitromethyl and dinitromethyl) to nitropyrazoles is essentially equivalent to introducing at least one -NO$_2$ (since one -NO$_2$ is used for the complete oxidation of the C atom in -CH$_3$) [56]. For the trinitromethyl group, it can be incorporated into N position or C position of nitropyrazoles with different energetic properties. The N-H bond of nitropyrazole is relatively active which could provide a reaction site for functionalization easily. In 2014, Yin et al. [57] obtained the carbon and nitrogen functionalization of nitropyrazole with N-trinitroethylaniline group (Figure 3, Scheme A). Thereby, 4-NP reacted with NH$_2$SO$_3$H acid and K$_2$CO$_3$ to accomplish amination, and after functionalization of amino group, the 1-amino-4-nitropyrazole underwent the Mannich reaction with trinitroethanol to get 4-nitro-N-(2,2,2-trinitroethyl)-1H-pyrazol-1-amine (1). In 2015, Dalinger et al. [58] prepared and characterized a nitropyrazole bearing a trinitromethyl moiety at N atom, 4-nitro-1-(trinitromethyl)-pyrazoles (2). They synthesized the target compound by a destructive nitration of 4-nitro-1-acetonylpyrazole with a mixture of concentrated HNO$_3$ and H$_2$SO$_4$ (Figure 3, Scheme B). Although the compound 1 was successfully synthesized, the yield was very low (28%) and this process was comparatively too time-consuming (15 d). To explore new high-performance EM, several C-trinitromethyl-substituted mononitropyrazoles have been reported. In 2018, Zhang and co-authors [56] first synthesized the C-trinitromethyl-substituted nitropyrazole (Figure 4, Scheme A). The reaction of 3-pyrazolecarbaldehyde oxime with N$_2$O$_4$ produced the 3-trinitromethylpyrazole and 1-nitro-3-trinitromethylpyrazole (3). They found that the increasing N$_2$O$_4$ concentration could improve the proportion of 3 and 3-trinitromethylpyrazole reacting with N$_2$O$_4$ also form 3, indicating N$_2$O$_4$ enable nitrate the N position of pyrazole. After the introduction of trinitromethyl group on C position, the 4-nitro-3-trinitromethylpyrazole (4) could be obtained with fuming nitric acid and oleum by -NO$_2$ rearrangement of 3 or nitration of 3-trinitromethylpyrazole. In 2019, Xiong et al. [59] further designed 3-Trinitromethyl-4-nitro-5-nitramine-1H-pyrazole (5). It was notable that the yield of 5 could improve with the concentration of HNO$_3$ increasing in the last nitration step of Scheme B (Figure 4). For the dinitromethyl group, Semenov et al. [60] prepared the 4-nitro-1-dinitromethylpyrazole by nitrating 4-nitro-1-acetonylpyrazole using H$_2$SO$_4$/H$_2$O mixture, and while the yield was low and it was not investigated as energetic material. In 2019, Pang et al. [61] introduced the dinitromethyl group into nitropyrazole and developed the salt, hydrazinium 5-nitro-3-dinitromethyl-2H-pyrazole (6), according to Scheme A in Figure 5. In 2020, Cheng et al. [62] synthesized 3-nitro-4-dinitromethyl-2H-pyrazole (7) and its salts, further exploring the application of dinitromethyl group in mononitropyrazole. Table 2 shows the energetic properties of the polynitromethyl-substituted mononitropyrazoles and salts compared with TNT and RDX. All the density of the derivatives of mononitropyrazole was higher than TNT and close to that of RDX, especially 7a showed the highest density. 3 and 5 owned the desirable detonation properties, while exhibited poor safety. It was notable that C-trinitromethyl-substituted derivatives owned higher heat of formation than those of N-trinitromethyl-substituted derivatives, and the derivatives with dinitromethyl group owned lower heat of formation than derivatives with trinitromethyl group. Most of the neutral derivatives hold low decomposition temperatures owing to the instability of the polynitromethyl moiety. Compound 4 had the highest decomposition temperature possibly because of the strong intermolecular hydrogen bonding interactions. By comparing 4 and 5, we can see the

| Explosive | $\rho$/g cm$^{-3}$ | $D$/km s$^{-1}$ | $P}$/GPa | $T_m$/°C | OB/°C | N/% | Ref. |
|-----------|------------------|---------------|----------|----------|------|-----|-----|
| 3-NP      | 1.57             | 7.02          | 20.08    | 174–175  | −77.88 | 37.17 | [55] |
| 4-NP      | 1.52             | 6.86          | 18.81    | 163–165  | −77.88 | 37.17 | [55] |
| 3-MNP     | 1.47             | 6.62          | 17.11    | 80–83    | −107.09 | 26.77 | [3]  |
| 4-MNP     | 1.40             | 6.42          | 15.52    | 82       | −107.09 | 26.77 | [3]  |
The nitramino group could further increase the power with low sensitivities. For the salts of compound 7, 7d with high detonation properties (comparing with RDX) and low sensitivities could serve as a promising candidate as a new high energy density oxidizer.

**Figure 3.** Synthesis of compounds 1 and 2.

**Figure 4.** Synthesis of compounds 3–5.

**Figure 5.** Synthesis of salts of trinitromethyl and dinitromethyl-substituted mononitropyrazoles.
Table 2. Properties of the derivatives of compounds 1–7.

| Entry | ρ/g cm⁻³ | D/km s⁻¹ | P/GPa | Tₘf/°C | Tₐf/°C | OB% | N% | HOF/kJ mol⁻¹ | IS/J | FS/N | Ref. |
|-------|---------|---------|-------|--------|--------|-----|----|-------------|------|------|------|
| 1     | 1.74    | 8.39    | 30.8  | 109.0  | 112    | +2.75 | 33.68 | 140.9 | 15.0 | 360 | [57] |
| 2     | 1.80    | 8.65    | 33.9  | 39.0   | 145    | -6.10 | 32.07 | 181.0 | 7.5  | 120 | [58] |
| 3     | 1.85    | 8.93    | 35.9  | 59.9   | 113    | +18.3 | 32.07 | 311.4 | 2.5  | 36  | [56] |
| 4     | 1.80    | 8.60    | 32.2  | 147.2  | 154    | +18.3 | 32.07 | 208.1 | 3.0  | 80  | [56] |
| 5     | 1.90    | 9.12    | 37.2  | 74     | 124    | +24.8 | 34.79 | 320.2 | 5.0  | 80  | [59] |
| 6     | 1.84    | 8.79    | 33.8  | -      | 128    | -9.64 | 39.35 | 194.8 | 7.0  | 192 | [61] |
| 7     | 1.76    | 8.53    | 30.8  | -      | 117    | -25.79 | 32.26 | 205.6 | 17.0 | 114 | [62] |
| 7a    | 2.01    | 8.13    | 29.5  | -      | 171    | -21.94 | 27.44 | 55.7  | 4.0  | 36  | [62] |
| 7b    | 1.87    | 8.26    | 28.6  | -      | 203    | -23.42 | 29.29 | 28.2  | 9.0  | 120 | [62] |
| 7c    | 1.78    | 8.60    | 33.0  | -      | 141    | -34.16 | 35.90 | 85.4  | >20.0 | 192 | [62] |
| 7d    | 1.80    | 8.70    | 34.1  | -      | 166    | -24.20 | 33.60 | 135.5 | >20.0 | 162 | [62] |
| 7e    | 1.72    | 8.26    | 28.7  | -      | 161    | -46.37 | 40.58 | 43.8  | >20.0 | 240 | [62] |
| 7f    | 1.71    | 8.48    | 30.1  | -      | 140    | -46.74 | 43.29 | 231.4 | >20.0 | 252 | [62] |
| TNT   | 1.65    | 6.88    | 19.5  | 80.5   | 295    | -73.8 | 18.49 | -67.0 | 15.0 | 358 | [62] |
| RDX   | 1.80    | 8.75    | 34.9  | 204.1  | 210    | -21.6 | 37.82 | 70.0  | 7.0  | 120 | [62] |

Connecting nitropyrazoles with nitrogen-rich compounds (including tetrazole, triazole, furazan, tetrazine, triazine, and others) has attracted more interest in many fields, it also be an effective approach to increasing the content of nitrogen and getting new high-performance energetic materials. In 2015, Yin et al. [63] synthesized energetic salts based on N-methyl 6-nitropyrazolo[3,4-d][1,2,3]triazol-3(4H)-olate in a similar manner exhibiting good detonation performance with relatively low sensitivities. In 2016, Dalinger et al. [64] synthesized and investigated systematically a series of 1- and 5-(pyrazolyl)tetrazole amino and nitro derivatives which could be components of dyes and luminophores, and high-energy materials. Some of them were always used as intermediates due to their poor energetic properties. In 2017, Zyuzin et al. [65] introduced the 2,2-bis(methoxy-NNO-azoxy)ethyl group to nitropyrazoles to increase the hydrogen content for some special application (gun propellants, solid rocket propellants and others). The derivatives of 3-NP and 4-NP showed high heat of formation, while the oxygen balances and calculated detonation velocity were not ideal. Then, Zyuzin et al. [66] further introduced the trinitromethyl moiety owning the most oxygen-rich block into the combination of tetrazole and pyrazole rings to obtain oxygen-balanced energetic materials with high nitrogen content (8–11) (Figure 6). In 2019, Tang et al. [67] developed several compounds and salts based 3,5-diamino-4-nitropyrazole functionalizing the with tetrazole group and triazine group (12–15) (Figure 7). As shown in Table 3, all the compounds had high density, high nitrogen content and good detonation properties, while the thermal stability of 12–15 was better than that of 8–11. In particular, the derivatives 12–15 showed excellent insensitivities. In addition, most compounds owned positive and high heat of formation, but the presence of water molecules in 13a result in its negative heat of formation. Considering the low sensitivities, good detonation properties, and high thermal stabilities, these derivatives with nitrogen-rich groups may be the candidates of insensitive high energetic materials.
**Figure 6.** Synthesis of mononitropyrazole derivatives 8–11.

**Figure 7.** Synthesis of mononitropyrazole derivatives 12–15.

**Table 3.** Energetic characteristics of compounds 8–15. The data of compounds 8–11 are from reference [66], the data of compounds 12–15 are from reference [67].

| Entry | $\rho$/g·cm$^{-3}$ | $D$/km·s$^{-1}$ | $P$/GPa | $T_d$/°C | N/% | HOF/kJ·mol$^{-1}$ | IS/J | FS/N |
|-------|-----------------|----------------|---------|----------|-----|------------------|------|------|
| 8     | 1.79            | 8.86           | 34      | 127      | 42.43 | 602              | -    | -    |
| 9     | 1.81            | 8.47           | 31      | 111      | 41.59 | 386              | -    | -    |
| 10    | 1.91            | 8.99           | 36      | 138      | 41.67 | 589              | -    | -    |
| 11    | 1.76            | 8.78           | 32      | 132      | 42.43 | 629              | -    | -    |
| 12    | 1.76            | 8.26           | 25.9    | 272      | 59.70 | 408              | 30   | 360  |
| 12a   | 1.78            | 8.82           | 29.9    | 187      | 56.89 | 445              | 32   | 360  |
| 12b   | 1.75            | 8.80           | 28.9    | 229      | 63.36 | 547              | 35   | >360 |
| 12c   | 1.70            | 8.29           | 24.9    | 251      | 61.39 | 399              | 40   | >360 |
| 12d   | 1.69            | 8.24           | 23.9    | 224      | 63.84 | 486              | 40   | >360 |
| 12e   | 1.72            | 8.14           | 23.6    | 287      | 63.21 | 338              | 40   | >360 |
| 13    | 1.72            | 8.00           | 22.8    | 200      | 52.96 | 127.6            | >40  | >360 |
| 13a   | 1.68            | 8.00           | 23.8    | 196      | 45.15 | -483.3           | 32   | 360  |
| 14    | 1.75            | 8.81           | 32.6    | 148      | 47.94 | 462.8            | 30   | 360  |
| 15    | 1.78            | 7.79           | 21.8    | 406      | 53.52 | 127.1            | >40  | >360 |
Moreover, nitrogen-rich heterocycles with a nitramino moiety could exhibit better performance than the corresponding nitro-substituted analogs as above mentioned [59,68]. In 2019, Shreeve and her group [69] reported a green synthetic route for high-performance nitramino nitropyrazoles. Figure 8 depicted the synthesis of corresponding derivatives, among them the 3,5-dinitramino-4-nitropyrazole (16) was quite sensitive to mechanical stimulation. From Table 4, the compound 16b showed promising properties with a high density (1.87 g·cm⁻³), good detonation properties (D of 9.58 km·s⁻¹ and P of 38.5 GPa), decomposition temperature of 194 °C, and acceptable sensitivities. Xu et al. [70] introduced nitramino and triazole groups into mononitropyrazole to construct multiple hydrogen bonds (17), and synthesized the 4-nitro-3,5-bis(1H-1,2,4-triazol-3-nitramino)-1H-pyrazole (19) and its ionic derivatives (19a–i) as shown in Figure 9. Table 4 also showed their energetic properties. Compound 17 had the highest decomposition temperature (353.6 °C) and excellent low sensitivity (IS > 40, FS > 360), indicating it could be used as heat-resistant insensitive explosive. The compounds (18–19i) exhibited moderate detonation properties, high positive heat of formation and ideal insensitivities which had great potential application in green and safe energetic materials. Ma et al. [71] also fused nitropyrazole with triazine and nitramino groups, and prepared a series of salts based on compounds 20 and 21 (Figure 10). These compounds owned high thermal stability and excellent insensitive properties because of the existence of triazine ring.

![Figure 8. Synthesis of compound 16 and its salts.](image-url)

Table 4. Energetic characteristics of compounds 16a–21d. The data of compounds 16a–d are from reference [69], the data of compounds 17–19i are from reference [70], the data of compounds 20a·H₂O–21d·H₂O are from reference [71].

| Entry | ρ/g·cm⁻³ | D/km·s⁻¹ | P/GPa | T₉₀/°C | HOF/kJ·mol⁻¹ | IS/J | FS/N |
|-------|----------|----------|-------|---------|-------------|------|------|
| 16a   | 1.90     | 9.39     | 40.0  | 155.0   | 74          | 6    | 120  |
| 16b   | 1.87     | 9.58     | 38.5  | 194.0   | 266         | 12   | 160  |
| 16c   | 1.80     | 8.84     | 32.6  | 192.0   | −20         | 15   | 240  |
| 16d   | 2.12     | 7.64     | 26.4  | 232.0   | 246         | 2    | 120  |
| 17    | 1.77     | 8.24     | 23.1  | 353.6   | 555.0       | >40  | >360 |
| 18    | 1.87     | 8.75     | 33.0  | 238.2   | 737.6       | 30   | 360  |
| 19    | 1.92     | 9.01     | 35.9  | 134.4   | 791.8       | 20   | 270  |
| 19a   | 1.76     | 8.68     | 30.0  | 186.6   | 711.4       | >40  | >360 |
| 19b   | 1.79     | 9.08     | 33.6  | 171.3   | 842.0       | >40  | >360 |
| 19c   | 1.73     | 8.76     | 30.2  | 186.6   | 1062.4      | >40  | >360 |
| 19d   | 1.71     | 8.19     | 25.1  | 195.4   | 677.9       | >40  | >360 |
| 19e   | 1.71     | 8.50     | 27.3  | 191.3   | 1068.7      | >40  | >360 |
| 19f   | 1.75     | 8.71     | 29.7  | 208.2   | 1014.6      | 22.4 | >360 |
| 19g   | 1.72     | 8.12     | 25.7  | 168.5   | 1300.5      | >40  | >360 |
| 19h   | 1.74     | 8.16     | 26.0  | 189.7   | 1270.5      | >40  | >360 |
| 19i   | 1.72     | 8.14     | 25.9  | 175.9   | 1511.2      | >40  | >360 |
| 20a   | 1.82     | 8.39     | 28.2  | 180.0   | 60.0        | 40   | 240  |
| 20b   | 1.83     | 8.10     | 28.0  | 279.0   | 105.0       | >40  | >360 |
| 21    | 1.89     | 8.71     | 31.9  | 248.0   | 314.6       | >40  | >360 |
| 21a·H₂O | 1.95   | 8.29     | 29.1  | 341.0   | 260.9       | >40  | >360 |
| 21b·H₂O | 1.81   | 8.98     | 32.1  | 218.0   | 386.2       | >40  | >360 |
| 21c·H₂O | 1.80   | 9.06     | 31.7  | 190.0   | 557.5       | >40  | >360 |
| 21d·H₂O | 1.60   | 8.22     | 24.6  | 223.0   | 690.0       | >40  | >360 |
In an earlier study, pyrazole, 4-NP, 3-nitro-4-cyanopyrazole and other raw materials have been investigated to prepare 3,4-DNP, while most of the methods did not satisfy industrialization due to low sensitivity (IS > 40, FS > 360), indicating it could be used as heat-resistant insensitive explosive. The introduction of poly nitromethyl group can improve the oxygen balance efficiently, while have a little influence on the heats of formation. The nitramino group and nitrogen-rich heterocyclic can enhance the detonation properties, improve the safety, and increase the heats of detonation. Moreover, nitrogen-rich heterocycles with a nitramino moiety could exhibit better performance than the corresponding nitro-substituted analogs as above mentioned [59, 68]. In 2019, Shreeve and her group [69] reported a green synthetic route for high-performance nitramino nitropyrazoles. These compounds owned high thermal stability and excellent insensitive properties because of the existence of triazine ring.

2.2. Dinitropyrazoles and Their Derivatives

Dinitropyrazoles own higher density and better detonation performance than mononitropyrazoles attributing to one more nitro group. The typical dinitropyrazoles include 3,4-dinitropyrazole (3,4-DNP), 3,5-dinitropyrazole (3,5-DNP), 1-methyl-3,4-dinitropyrazole (3,4-MDNP), 1-methyl-3,5-dinitropyrazole (3,5-MDNP), and 4-amino-3,5-dinitropyrazole (LLM-116).

3,4-DNP is a kind of white crystal, possessing higher density (1.87 g·cm⁻³), lower melting point (86–88 °C), higher decomposition temperature (285 °C), higher detonation velocity (8.1 km·s⁻¹) and detonation pressure (29.4 GPa) than TNT. This compound was first reported by Biffin’s team in 1966 [72]. In an earlier study, pyrazole, 4-NP, 3-nitro-4-cyanopyrazole and other raw materials have been investigated to prepare 3,4-DNP, while most of the methods did not satisfied industrialization due

![Figure 8. Synthesis of compound 16 and its salts.](image_url)

![Figure 9. Synthesis of compounds 17–19i.](image_url)

![Figure 10. Synthesis of compounds 20a–21d.](image_url)
to complex process, high production cost or low yield [45,55,73–76]. At present, the three-step synthetic route as shown in Figure 11 (Scheme A), and the two-step route (Scheme B) are the most widely used [77–80]. 3,4-MDNP is a typical thermal stability nitropyrazole, exhibiting stable thermodynamic state at 300 °C. Its melting point and density are lower than those of 3,4-DNP (20–23 °C, 1.67 g·cm⁻³), and 3,4-DNP shows low detonation velocity (7.76 km·s⁻¹) and detonation pressure (25.57 GPa) due to the introduction of methyl group. It has potential application in liquid explosive, which can reduce the melting point of liquid phase carrier in castable explosive [32]. Recently, Ravi et al. [73] had synthesized 3,4-MDNP by nitrating 1-methylpyrazole or 1-methyl-3-nitropyrazole with montmorillonite (K-10) and Bi(NO₃)₃, while this method was high cost and the products were difficult to separate. Li et al. [81] reacted 3,4-DNP and dimethyl carbonate (DMC) in DMF with K₂CO₃ as catalyst, then, his group further synthesized 3,4-MDNP with 3-NP as raw material (Figure 11, Scheme C) [82]. In this method, DMC was used as methylation agent and the yield of methylation was high (95.6%), which could meet the requirement of green chemistry. As 3,5-DNP with a melting point of 173–174 °C and density of 1.80 g·cm⁻³, the decomposition temperature of 316.8 °C owns higher detonation properties than 3,4-DNP (7.76 km·s⁻¹ and 25.57 GPa). Moreover, 3,5-DNP is relatively stable because of the symmetrical molecular distribution, it can be used as a simple explosive or as a key intermediate in the synthesis of insensitive explosives [55]. Generally, the starting materials for preparing 3,5-DNP could be pyrazole and 3-NP. Wang et al. [83] nitrated 3-NP to get 1,3-dinitropyrazole, then 1,3-dinitropyrazole was reacted with NH₃ in PhCN to produce the ammonium salt of 3,5-DNP. After neutralization with hydrochloric acid, the 3,5-DNP could be obtained (Figure 12, Scheme A). Liu et al. [28] also nitrated 3-NP, and rearranged 1,3-dinitropyrazole to get 3,5-DNP (Figure 12, Scheme B). For pyrazole as starting material, 3,5-DNP was always prepared by a four-step route (nitration of pyrazole, rearrangement of N-nitropyrazole, nitration of 3-NP, and rearrangement of 1,3-dinitropyrazole). 3,5-MDNP owns the similar energetic properties with 3,4-MDNP, while it has a higher melting point (about 60 °C). Moreover, 3,5-MDNP could be synthesized by methylation of 3,5-DNP [84]. However, most methylation agents were extremely toxic, thus searching for a green methylation agent would be the key factor.

![Figure 11. Synthesis of 3,4-DNP and 3,4-MDNP.](image-url)

LLM-116 is a powerful and insensitive explosive, its energy is 90% of HMX and its impact sensitivity is extremely low [55,85]. It was first synthesized by the Lawrence Livermore National Laboratory (LLNL) in 2001, and many studies were performed to assess its synthesis in the following years. Wang et al. [86] utilized vicarious nucleophilic substitution (VNS) of 3,5-DNP and trimethylhydrazine iodide (TMHI) to prepare LLM-116 with a yield of 60%, while the toxic TMHI was the main factors restricting wide application of this method. In 2014, Stefan et al. [87] developed four synthetic routes of LLM-116, using 4-NP, 3,5-dimethylpyrazole, 3,5-DNP and 4-chloropyrazole as starting materials, respectively (Figure 13, Scheme A–D). Table 5 shows the comparison of the four routes. The synthesis of...
Scheme D was simple and its yield was high, which was suitable for industrialization. Zhang et al. [88] also used 4-chloropyrazole as a starting material to synthesize LLM-116 with an overall yield of 65%.

![Synthesis of 3,5-DNP and 3,5-MDNP.](image)

**Figure 12.** Synthesis of 3,5-DNP and 3,5-MDNP.

LLM-116 is a powerful and insensitive explosive, its energy is 90% of HMX and its impact sensitivity is extremely low [55,85]. It was first synthesized by the Lawrence Livermore National Laboratory (LLNL) in 2001, and many studies were performed to assess its synthesis in the following years. Wang et al. [86] utilized vicarious nucleophilic substitution (VNS) of 3,5-DNP and trimethylhydrazine iodide (TMHI) to prepare LLM-116 with a yield of 60%, while the toxic TMHI was the main factor restricting wide application of this method. In 2014, Stefan et al. [87] developed four synthetic routes of LLM-116, using 4-NP, 3,5-dimethylpyrazole, 3,5-DNP and 4-chloropyrazole as starting materials, respectively (Figure 13, Scheme A–D). Table 5 shows the comparison of the four routes. The synthesis of Scheme D was simple and its yield was high, which was suitable for industrialization. Zhang et al. [88] also used 4-chloropyrazole as a starting material to synthesize LLM-116 with an overall yield of 65%.

![Synthesis of LLM-116.](image)

**Figure 13.** Synthesis of LLM-116.

**Table 5.** A brief comparison of four routes by Stefan.

|                  | Via 4-NP (Method A) | Via 3,5-Dimethylpyrazole (Method B) | Via 3,5-DNP (Method C) | Via 4-Chloropyrazole (Method D) |
|------------------|---------------------|-------------------------------------|------------------------|--------------------------------|
| Four steps       | 4                    | 6                                   | 5                      | 2                              |
| Moderate amount of waste | Moderate amount of waste | Moderate amount of waste | Moderate amount of waste | Small amount of waste |
| No unfavorable solvents required | No unfavorable solvents required | DMSO used in the last step | No unfavorable solvents required |                        |
| Moderate overall yield, 40% | Moderate overall yield, 37% | Low overall yield, 21% | Moderate overall yield, 61% |                 |
| Average yield/step: 80% | Average yield/step: 85% | Average yield/step: 73% | Average yield/step: 78% |                        |

In addition, 4-Chloro-3,5-dinitropyrazole was a useful intermediate in the preparation of various 3,5-DNP [89], owning good reactivity towards nucleophiles. He et al. [90] synthesized a series of 3,5-DNP derivatives based on 4-chloro-3,5-dinitropyrazole and 1-methyl-4-chloro-3,5-dinitropyrazole shown in Figure 14. From Table 6, all compounds exhibited better detonation properties than those of TNT, and these compounds owned better IS than RDX except compound 33. Compounds 26 and 28
had an especially good balance between physical properties and detonation properties as well as excellent insensitivity, making them potential replacement of RDX.

Molecules 2020, 25, x FOR PEER REVIEW

No unfavorable solvents required

DMSO used in the last step

Moderate overall yield, 40% Moderate overall yield, 37% Low overall yield, 21%

Average yield/step: 80% Average yield/step: 85% Average yield/step: 73% Average yield/step: 78%

In addition, 4-Chloro-3,5-dinitropyrazole was a useful intermediate in the preparation of various 3,5-DNP [89], owning good reactivity towards nucleophiles. He et al. [90] synthesized a series of 3,5-DNP derivatives based on 4-chloro-3,5-dinitropyrazole and 1-methyl-4-chloro-3,5-dinitropyrazole shown in Figure 14. From Table 6, all compounds exhibited better detonation properties than those of TNT, and these compounds owned better IS than RDX except compound 33. Compounds 26 and 28 had an especially good balance between physical properties and detonation properties as well as excellent insensitivity, making them potential replacement of RDX.

Figure 14. Synthesis of derivatives based on 4-amino-3,5-dinitropyrazole and 1-methyl-4-chloro-3,5-dinitropyrazole.

Table 6. Physical and detonation properties of compounds 22–35. The data of compounds 22–35 are from reference [90].

| Entry | ρ/g cm⁻³ | D/km s⁻¹ | P/GPa | Td/°C | HOF/kJ mol⁻¹ | IS/J |
|-------|----------|----------|-------|-------|---------------|------|
| 22    | 1.74     | 8.22     | 30.1  | 178   | 137.0         | 17   |
| 23    | 1.69     | 8.25     | 28.7  | 176   | 104.6         | 35   |
| 24    | 1.72     | 8.31     | 30.2  | 176   | 220.7         | 18   |
| 25    | 1.63     | 8.14     | 26.3  | 275   | 64.8          | >60  |
| 26    | 1.88     | 8.73     | 35.0  | 241   | 166.0         | >40  |
| 27    | 1.66     | 7.82     | 23.4  | 245   | 133.5         | >40  |
| 28    | 1.84     | 8.46     | 31.0  | 308   | 182.6         | >40  |
| 29    | 1.78     | 8.39     | 31.4  | 233   | 236.6         | 10   |
| 30    | 1.74     | 8.41     | 31.0  | 161   | 436.0         | 14   |
| 31    | 1.63     | 7.42     | 21.7  | 228   | 177.0         | 22   |
| 32    | 1.71     | 8.72     | 30.9  | 146   | 549.6         | 8    |
| 33    | 1.70     | 8.18     | 27.6  | 101   | 414.4         | 6    |
| 34    | 1.67     | 7.80     | 24.6  | 270   | 64.5          | >40  |
| 35    | 1.78     | 8.25     | 31.2  | 285   | 109.1         | >40  |

Energetic salts often possess superior properties comparing with non-ionic species since they always show lower vapor pressures, lower impact and friction sensitivities, and enhanced thermal stabilities [19]. In addition to the derivatives mentioned above, Klapötke group [26] developed the ionic salts of 3,4-DNP and 3,5-DNP shown in Figure 15, and these salts were extremely insensitive in Table 7. Comparing with 3,4-DNP, 36 and 38 owned much lower decomposition temperatures, similar to that
of 37, 39 and 3,5-DNP. Zhang et al. [91] developed the ionic salts of LLM-116 with several nitrogen-rich cations as shown in Figure 16. These compounds showed extraordinary insensitivity to impact (>60 J), as the detonation properties of 40i and 41k were comparable to those of TATB (31.15 GPa, 8.11 km·s⁻¹) (Table 7).

**Figure 15.** Synthesis of ionic salts of 3,4-DNP and 3,5-DNP.

**Table 7.** Physical and detonation properties of ionic salts of dinitropyrazoles. The data of compounds 36–39 are from reference [26], the data of compounds 40a–41o and TATB are from reference [91].

| Entry | ρ/g cm⁻³ | D/km·s⁻¹ | P/GPa | Td/°C | HOF/kJ·mol⁻¹ | IS/J | FS/N |
|-------|----------|----------|-------|-------|--------------|------|------|
| 36    | 1.69     | -        | -     | 127   | -            | 40   | 360  |
| 37    | 1.70     | 8.11     | 25.9  | 300   | -            | 40   | 360  |
| 38    | 1.63     | 7.59     | 21.1  | 156   | -            | 40   | 360  |
| 39    | 1.59     | 7.32     | 19.1  | 295   | -            | 40   | 360  |
| 40a   | 1.63     | 8.14     | 26.3  | 275   | 64.8         | >60  | -    |
| 40b   | 1.64     | 8.19     | 26.4  | 221   | 222.6        | >60  | -    |
| 40c   | 1.63     | 7.72     | 21.6  | 303   | 36.1         | >60  | -    |
| 40d   | 1.69     | 8.24     | 25.2  | 223   | 140.1        | >60  | -    |
| 40e   | 1.62     | 7.44     | 22.7  | 179   | 310.4        | >60  | -    |
| 40f   | 1.67     | 7.73     | 22.4  | 257   | 283.6        | >60  | -    |
| 40g   | 1.73     | 8.12     | 25.8  | 223   | 411.1        | >60  | -    |
| 40h   | 1.79     | 8.42     | 27.2  | 270   | 241.6        | >60  | -    |
| 40i   | 1.84     | 8.74     | 32.6  | 193   | 211.9        | >60  | -    |
| 41j   | 1.67     | 8.35     | 25.9  | 201   | 250.5        | >60  | -    |
| 41k   | 1.71     | 8.75     | 28.9  | 229   | 356.9        | >60  | -    |
| 41l   | 1.72     | 7.98     | 24.2  | 169   | 100.4        | >60  | -    |
| 41m   | 1.73     | 7.94     | 23.1  | 243   | -166.3       | >60  | -    |
| 41n   | 1.54     | 7.71     | 21.0  | 206   | 389.3        | >60  | -    |
| 41o   | 1.60     | 7.78     | 22.4  | 173   | 471.8        | >60  | -    |
| TATB  | 1.93     | 8.11     | 31.2  | 324   | -140.0       | 50   | -    |

*N*-oxidation of nitrogen-rich heterocycles including transformation of amino group to nitroso, azoxy, or nitro groups is another approach to designing HEDMs, which opens new avenues for the development of HEDMs [92,93]. The efforts to developing *N*-oxidation of dinitropyrazoles have been made recently. Bölter et al. [94] introduced -OH on N atom of 3,4-DNP and 3,5-DNP, and obtained several salts (Figure 17, Scheme A). From Table 8, these compounds were less sensitive than RDX, and did not exhibited excellent detonation properties. Yin et al. [95] synthesized a family of 4-amino-3,5-dinitro-1H-pyrazol-1-ol (44) and its ionic derivatives (44a–f) (Figure 17, Scheme B). Except 44·H₂O, all the compounds (44a–f, and 45) with thermal decomposition temperatures (169–216 °C) shown good balance between detonation properties and insensitive properties as shown in Table 8. Zhang et al. [96] synthesized the 4-nitramino-3,5-dinitropyrazole by nitrating the -NH₂ of LLM-116, and prepared several energetic salts which exhibited good insensitivity and moderate detonation properties.
remarkable improvements in densities and detonation properties of energetic materials. Especially the molecules of TATB (31.15 GPa, 8.11 km·s\(^{-1}\)) showed extraordinary insensitivity to impact (>60 J), as the detonation properties of several nitrogen-rich cations shown in Figure 16. These compounds showed extraordinary properties, and did not exhibit excellent detonation properties. Yin et al. [95] synthesized a family of 4-amino-3,5-dinitro-1-azoxy, or nitro groups is another approach to designing HEDMs, which opens new avenues for the design of energetic salts that possess superior properties. Bölter et al. [94] introduced -OH on the azoxy, or nitro groups.

As mentioned above, polynitromethyl are considered to be more favorable groups to give remarkable improvements in densities and detonation properties of energetic materials. Especially the

| Entry | \(\rho\)/g cm\(^{-3}\) | \(D\)/km·s\(^{-1}\) | \(P\)/GPa | \(T_d\)/°C | IS/J | FS/N |
|-------|-----------------|-----------------|--------|----------|------|------|
| 42a   | 1.96            | 7.92            | 26.9   | 197      | 5    | 216  |
| 42b   | 1.68            | 8.28            | 28.2   | 167      | 10   | 360  |
| 42c   | 1.70            | 8.06            | 25.1   | 180      | 30   | 360  |
| 42d   | 1.64            | 8.02            | 24.7   | 169      | 10   | 360  |
| 43a   | -               | -               | -      | 229      | 6    | 240  |
| 43b   | 1.62            | 7.91            | 24.4   | 224      | 30   | 288  |
| 43c   | 1.68            | 7.94            | 24.2   | 266      | 40   | 360  |
| 43d   | 1.68            | 8.16            | 25.7   | 131      | 10   | 360  |
| 44-H_2O | 1.86        | -               | -      | 93       | 20   | 240  |
| 44a   | 1.79            | 8.94            | 34.4   | 216      | 25   | 240  |
| 44b   | 1.86            | 9.00            | 37.6   | 182      | 35   | 360  |
| 44c   | 1.84            | 8.80            | 34.0   | 175      | 40   | 360  |
| 44d   | 1.71            | 8.20            | 26.4   | 204      | 40   | 360  |
| 44e   | 1.71            | 8.54            | 28.0   | 169      | 40   | 360  |
| 44f   | 175             | 8.88            | 30.7   | 214      | 40   | 360  |
| 45    | 1.80            | 8.81            | 33.9   | 212      | 40   | 360  |

As mentioned above, polynitromethyl are considered to be more favorable groups to give remarkable improvements in densities and detonation properties of energetic materials. Especially the
N-trinitroethylamination of nitropyrazole is more available since it is stable to be handled safely. The N-trinitroethylamination of dinitropyrazole was firstly proposed by Shreeve team [57]. They obtained several N-amino-dinitropyrazoles firstly, then these compounds underwent Mannich reactions with trinitroethanol to acquire the corresponding derivatives (46–50) (Figure 18, Scheme A). It was noteworthy that 1-amino-3,5-dinitropyrazole and 1-amino-3,4-dinitro-5-cyanopyrazole failed to get the corresponding compounds due to the electron-withdrawing effect of substituent groups bonded to dinitropyrazole ring. In addition, they employed an alternative synthetic method to obtain 1,5-diamino-3,4-dinitropyrazole (51) (Figure 18, Scheme B) because attempted amination of this compound using TsONH2 acid or NH2OSO3H failed. From Table 9, although the azido-functionalized dinitropyrazole (47) decomposed at 121 °C, compound 46 and 51 had high decomposition temperatures, and 47 and 50–52 owned higher density than RDX. These indicated the introduction of an -NH2 could enhance density. In addition, N-trinitroethylamination of dinitropyrazole (48–50 and 52) shown high HOF and good detonation properties. N-trinitromethyl moiety was introduced by Dalinger’s team [58], they synthesized 3,4-dinitro-1-(trinitromethyl)-pyrazoles (53) and 3,5-dinitro-1-(trinitromethyl)-pyrazoles (54) with excellent physical and computational properties as shown in Figure 19. They were a little less insensitive than the RDX and PETN, similar to N-trinitroethylamination dinitropyrazoles shown in Table 9. Fluorine and fluorinated functional groups are importantly promising substituents in the field of energetic materials [97]. C(NO2)2F and C(NO2)2NF2 moieties bring high energy, maintaining high density and good thermal property were incorporated into dinitropyrazole by fluorinated compound 55 (Figure 19, Scheme C). The two compounds had high density (≥1.92 g·cm−3), good oxygen balance (+2.55% for 57 and 0% for 56), and high detonation pressure and velocity [98].

**Figure 18.** N-Trinitroethylamination of dinitropyrazole.

**Table 9.** Physical and computational properties of several polynitropyrazoles. The data of compounds 46–52 are from reference [57], the data of compounds 53–54 are from reference [58].

| Entry | ρ/g·cm−3 | D/km·s−1 | P/GPa | Tml/°C | T4l/°C | HOF/[kJ·mol−1] | IS/J | FS/N |
|-------|----------|----------|-------|--------|--------|----------------|------|------|
| 46    | 1.71     | 7.46     | 20.1  | 58     | 241    | 200.3          | >40  | 360  |
| 47    | 1.82     | 9.05     | 35.8  | 120    | 121    | 548.2          | 1.5  | 5    |
| 48    | 1.78     | 8.67     | 33.1  | 87     | 110    | 142.3          | 6    | 80   |
| 49    | 1.82     | 9.00     | 35.6  | -      | 117    | 491.7          | 2.5  | 20   |
| 50    | 1.81     | 9.75     | 34.3  | -      | 116    | 124.1          | 12   | 120  |
| 51    | 1.82     | 9.69     | 32.8  | 133    | 238.2  | 173.0          | >40  | 360  |
| 52    | 1.83     | 8.80     | 35.0  | -      | 134.4  | 112.0          | 8    | 80   |
| 53    | 1.91     | 8.67     | 35.5  | 80     | 157    | 244.0          | 8    | 130  |
| 54    | 1.94     | 8.73     | 36.6  | 81     | 159    | 206.0          | 9    | 145  |
Dinitropyrazoles bearing other heterocycles are also interesting and notable. To obtain the melt-castable explosives with good compatibility, improved oxygen balance and moderate detonation properties, compound 58 incorporating both N-trinitromethyl and C-methyl substituents in addition to nitro groups was synthesized by Sheremetev’s group [99] (Figure 20). This low melting temperature compound has been proved to own higher detonation pressure and velocity values than those of others melt-castable energetic heterocycles bearing methyl group, which provided feasible route to castable energetic materials. In addition, introduction of polynitrogen heterocycle and formation of energetic salts are main methods to improve the thermal stability of explosives [100]. In 2016, a heat-resistant energetic material, compound 59 bearing triazole ring, was synthesized using 5-amino-3-nitro-1H-1,2,4-triazole (ANTA) and 3,4,5-trinitrated-1H-pyrazole (TNP), and several salts based on it were developed by Zhou et al. [101] (Figure 21, Scheme A). As shown in Table 10, compound 59 had high decomposition temperature (270 °C) and high positive HOF (833 kJ·mol\(^{-1}\)). All the salts showed good thermal stability, excellent insensitivity, and good detonation properties. In particular, the guanidinium salt 59d exhibited the best thermal stability superior than that of most explosives. Considering thermal stability and energetic properties, compounds 59 and 59d could be used as heat-resistant explosives and it was possible that these compounds can be applied as heat-resistant materials. Afterwards, their group reported a family of unsymmetrical N-bridged dinitropyrazoles synthesized by TNP and 5-amino-1H-tetrazole (ATZ) and its organic salts (Figure 21, Scheme B). Several compounds (60, 60b, and 60c) with high N contents exhibited superior detonation velocities but inferior detonation pressures compared to HMX and insensitivities to impact (IS > 40 J) and friction (FS > 360 N) comparable to those of TATB (Table 10), which could be promising insensitive HEDMs for practical application.

![Figure 19. Synthesis of compounds 53–57.](image)

![Figure 20. Synthesis of compound 58.](image)
Scheme B). Several compounds (60, 60b, and 60c) with high N contents exhibited superior detonation velocities but inferior detonation pressures compared to HMX and insensitivities to impact (IS > 40 J) and friction (FS > 360 N) comparable to those of TATB (Table 10), which could be promising insensitive HEDMs for practical application.

**Table 10.** Physical and computational properties of 59–60i. The data of compounds 59–59m are from reference [101], the data of compounds 60–60i and HMX are from reference [88].

| Entry | ρ/g·cm⁻³ | D/km·s⁻¹ | P/GPa | N/% | Td/°C | HOF/kJ·mol⁻¹ | IS/J | FS/N |
|-------|----------|----------|-------|-----|-------|--------------|------|------|
| 59    | 1.84     | 9.17     | 37.8  | 44.2| 270   | 833.4        | 9    | 240  |
| 59a   | 1.73     | 8.62     | 31.6  | 46.4| 285   | 622.8        | >40  | >360 |
| 59b   | 1.76     | 8.83     | 34.4  | 44.0| 215   | 709.9        | 33   | 252  |
| 59c   | 1.74     | 8.80     | 32.9  | 48.6| 241   | 811.4        | >40  | >360 |
| 59d   | 1.78     | 8.66     | 31.1  | 48.8| 340   | 624.1        | >40  | >360 |
| 59e   | 1.65     | 8.24     | 26.5  | 50.7| 281   | 728.9        | >40  | >360 |
| 59f   | 1.70     | 8.54     | 28.9  | 52.4| 262   | 831.7        | 27   | 240  |
| 59g   | 1.71     | 8.69     | 30.0  | 54.0| 242   | 941.4        | 20   | 216  |
| 59h   | 1.72     | 8.36     | 28.8  | 51.0| 279   | 828.3        | >40  | 252  |
| 59i   | 1.74     | 8.56     | 29.5  | 52.6| 292   | 944.8        | >40  | >360 |
| 59j   | 1.80     | 9.03     | 35.2  | 54.5| 222   | 1211.7       | 12   | 252  |
| 59k   | 1.77     | 8.65     | 30.5  | 54.2| 303   | 1161.6       | 20   | >360 |
| 59l   | 1.75     | -        | -     | 41.0| 261   | -            | 7.5  | 252  |
| 59m   | 1.91     | -        | -     | 37.7| 281   | -            | 5    | 216  |
| 60    | 1.86     | 9.29     | 38.6  | 52.3| 279   | 856.4        | 35   | 240  |
| 60a   | 1.79     | 8.95     | 33.3  | 54.3| 299   | 672.6        | >40  | 168  |
| 60b   | 1.84     | 9.23     | 37.4  | 51.1| 296   | 719.7        | >40  | 216  |
| 60c   | 1.84     | 9.36     | 37.0  | 56.4| 290   | 819.8        | >40  | 360  |
| 60d   | 1.67     | 8.26     | 25.9  | 56.0| 256   | 648.8        | >40  | 360  |
| 60e   | 1.72     | 8.76     | 28.6  | 61.2| 216   | 808.7        | >40  | 32   |
| 60f   | 1.79     | 9.07     | 32.5  | 59.4| 285   | 844.9        | >40  | 288  |
| 60g   | 1.81     | 9.29     | 34.2  | 60.9| 287   | 954.9        | >40  | 84   |
| 60h   | 1.84     | 8.95     | 32.2  | 57.6| 286   | 840.2        | >40  | 360  |
| 60i   | 1.82     | 9.00     | 32.3  | 59.1| 261   | 960.0        | >40  | 360  |
| HMX   | 1.91     | 9.19     | 39.7  | 37.8| 287   | 104.8        | 7.4  | 120  |

Figure 21. Synthesis of compounds 59–60i.
In summary, some dinitropyrazoles and derivatives exhibit low melting points and high decomposition temperatures as well as good detonation, which can make them competitive candidates for a castable explosive. To further improve the performance of dinitropyrazole-based energetic materials, a combination of several functional groups should be better, for example, the combination of nitramine and polynitrogen heterocyclic which can endow them with high thermal stability and good detonation performance.

2.3. Trinitropyrazole and Its Derivatives

TNP is the unique pyrazole compound by total carbon nitrification [102]. This compound owns good thermal stability (260–350 °C of $T_d$) and chemical stability, and shows high detonation velocity (9.0 km·s$^{-1}$) and detonation pressure (37.09 GPa). Wu et al. reviewed the synthesis of TNP in recent years in detail [102], including direct nitration methods, amino oxidation method, amino diazotization method, iodo nitrification method and microwave rearrangement method. The typical synthesis of TNP is the oxidation of LLM-116 rather than 5-amino-3,4-dinitropyrazole, and this is partly because the amino group in LLM-116 has higher electron cloud density and steric hindrance than amino group in 5-amino-3,4-dinitropyrazole, which can promote the intermolecular oxidation reaction and avoid the occurrence of intermolecular side reaction effectively, and partly because the “NO$_2$-NH$_2$-NO$_2$” framework in LLM-116 makes it more stable and easier to synthesize. In addition, the nitrification of 3,5-DNP is another typical synthesis route of TNP. Traditional oxidation methods have the following defects: harsh reaction conditions, poor selectivity, by-products, high risk factor, expensive metal catalyst and toxic organic solvent. Although the synthesis of TNP with LLM-116 and 3,5-DNP as starting materials are mature, the synthesis of LLM-116 and 3,5-DNP are complicated. It is necessary to explore novel synthesis method. Zhao et al. [44] used LLM-116 as starting material, water as solvent, and KHSO$_5$ as oxidant to synthesize TNP. Ravi et al. [103] put forward the nitration system of metal nitrate and studied the process of nitration to TNP. These two methods are promising to prepare TNP.

Moreover, 1-methyl-3,4,5-trinitropyrazole (MTNP), a derivative of TNP, is an insensitive energetic material with 91.5 °C of melting point, 248–280 °C of decomposition temperature, 8.65 km·s$^{-1}$ of detonation velocity, and 33.7 GPa of detonation pressure [104]. Ravi et al. [103] added K-10 and TNP to bismuth impregnated in THF to obtain MTNP (Figure 22, Scheme A). There were also many routes to synthesize MTNP. Dalinger et al. [105,106] dissolved TNP in NaHCO$_3$ aqueous solution with Me$_2$SO$_4$ as methylation reagent to acquire MTNP (Figure 22, Scheme B). Guo et al. [107] synthesized MTNP from 1-methyl-pyrazole by one-step method with nitric acid and fuming sulfuric acid (Figure 22, Scheme C). Among these methods, selection of highly efficient catalytic synthesis process and low toxicity methylation reagent are the trend in MTNP synthesis. In addition, 1-amino-3,4,5-trinitropyrazole (ATNP) is also a derivative of TNP with excellent detonation properties ($D = 9.17$ km·s$^{-1}$ and $P = 40.9$ GPa) and thermal stability [108]. Ravi et al. [93] reported the synthesis route is shown in Scheme D of Figure 22 (Pic-O-NH$_2$ = 2,4,6-trinitrophenyl-O-hydroxylamine) with a yield of 26%.

The N-H bond in TNP is easy to neutralize with alkali or react with metal salts forming energetic salts due to the stereoscopic structure and spatial effect of pyrazole ring. These energetic salts further broaden the application of TNP. Zhang et al. [109] prepared a series of energetic salts of TNP based on nitrogen-rich cations (61a–m) (Figure 23, Scheme A), all the salts showed poorer densities and detonation properties than TNP (Table 11), but they owned good thermal stability and excellent insensitivity. Drukenmuller et al. [110] reported the synthesis of alkali and earth alkalii trinitropyrazolate (62a–d) (Figure 23, Scheme B), compound 62d exhibited predominantly decomposition temperatures (Table 11). They also prepared pyrotechnic formulations using 62c and 62d, which showed good color properties and low sensitivity as well as high $T_d$. In addition, Shreeve’s group [111] synthesized 3,4,5-trinitropyrazole-1-ol (63) and its nitrogen-rich salts (63a–g) (Figure 24) the corresponding properties are shown in Table 11. Compound 63 with its high oxygen content (51.13%) could be the green replacement of the currently used oxidizer (NH$_4$ClO$_4$), while the high IS
(1 J) restricted its application. Compound 63a–g with acceptable impact sensitivities and detonation performance could be useful energetic materials.

Figure 22. Synthesis of MTNP and ATNP.

Figure 23. Synthesis of different salts of TNP. (A), the polynitrogen salts; (B), the alkali and earth alkali salts.

Table 11. Property parameters of salts of TNP. The data of compounds 61a–61m are from reference [109], the data of compounds 62a–62d are from reference [110], the data of compounds 63–63g are from reference [111].

| Entry | ρ/ g·cm⁻³ | D/ km·s⁻¹ | P/ GPa | Td/ °C | СHOF/ kJ·mol⁻¹ | IS/ J | FS/ N |
|-------|-----------|----------|--------|-------|---------------|------|-------|
| 61a   | 1.73      | 8.46     | 29.9   | 224   | 60.5          | 40   | -     |
| 61b   | 1.69      | 7.87     | 25.6   | 167   | 299.0         | >40  | -     |
| 61c   | 1.71      | 7.97     | 26.0   | 171   | 273.5         | >40  | -     |
| 61d   | 1.77      | 8.54     | 31.9   | 168   | 401.2         | >40  | -     |
| 61e   | 1.76      | 8.22     | 27.7   | 196   | 235.6         | >40  | -     |
| 61f   | 1.66      | 7.87     | 24.7   | 235   | 28.3          | >40  | -     |
| 61g   | 1.69      | 8.13     | 26.9   | 222   | 133.6         | >40  | -     |
| 61h   | 1.68      | 7.82     | 24.3   | 243   | 452.3         | >40  | -     |
Table 11. Property parameters of salts of TNP. The data of compounds 61a–61m are from reference [109], the data of compounds 62a–62d are from reference [110], the data of compounds 63–63g are from reference [111].

| Entry | $\rho$/g·cm$^{-3}$ | $D$/km·s$^{-1}$ | $P$/GPa | $T_{d}$/°C | HOF/kJ·mol$^{-1}$ | IS/J | FS/N |
|-------|------------------|----------------|---------|----------|-----------------|------|------|
| 61a   | 1.73             | 8.46           | 29.9    | 224      | 60.5            | 40   | -    |
| 61b   | 1.69             | 7.87           | 25.6    | 167      | 299.0           | >40  | -    |
| 61c   | 1.71             | 7.97           | 26.0    | 171      | 273.5           | >40  | -    |
| 61d   | 1.77             | 8.54           | 31.9    | 168      | 401.2           | >40  | -    |
| 61e   | 1.76             | 8.22           | 27.7    | 196      | 235.6           | >40  | -    |
| 61f   | 1.66             | 7.87           | 24.7    | 235      | 28.3            | >40  | -    |
| 61g   | 1.69             | 8.13           | 26.9    | 222      | 133.6           | >40  | -    |
| 61h   | 1.68             | 7.82           | 24.3    | 243      | 452.3           | >40  | -    |
| 61i   | 1.76             | 8.36           | 28.8    | 206      | 355.0           | >40  | -    |
| 61j   | 1.61             | 7.59           | 23.7    | 219      | 375.0           | >40  | -    |
| 61k   | 1.64             | 7.92           | 25.2    | 167      | 459.8           | 35   | -    |
| 61l   | 1.62             | 7.98           | 25.3    | 197      | 246.5           | >40  | -    |
| 61m   | 1.65             | 8.24           | 27.2    | 184      | 352.7           | >40  | -    |
| 62a   | -                | -              | -       | 274      | -               | 40   | 96   |
| 62b   | -                | -              | -       | 254      | -               | 25   | 80   |
| 62c   | -                | -              | -       | 193      | -               | 40   | 80   |
| 62d   | -                | -              | -       | 302      | -               | 5    | 144  |
| 63    | 1.90             | 8.67           | 36.4    | 146      | 118.5           | 1    | -    |
| 63a   | 1.82             | 8.68           | 35.1    | 176      | 35.1            | 6    | -    |
| 63b   | 1.72             | 8.18           | 28.8    | 171      | 3.1             | >40  | -    |
| 63c   | 1.73             | 8.18           | 29.5    | 140      | 274.9           | >40  | -    |
| 63d   | 1.73             | 8.18           | 29.2    | 132      | 250.5           | >40  | -    |
| 63e   | 1.74             | 8.15           | 30.8    | 118      | 381.6           | >40  | -    |
| 63f   | 1.76             | 8.26           | 29.7    | 186      | 213.7           | >40  | -    |
| 63g   | 1.77             | 8.44           | 31.1    | 185      | 331.9           | >40  | -    |

Polynitrogen heterocycle linking to TNP is a promising method to reach a balance between the energetic and physical properties of TNP, while there are a few references about it. Shreeve et al. [112] reported the synthesis of asymmetric $N,N'$-ethylene bridged 5-aminotetrazole and TNP moieties. They prepared 1-(2-(3,4,5-trinitro-1$H$-pyrazol-1-yl)ethyl)-1$H$-tetrazol-5-amine and 1-(3-(3,4,5-trinitro-1$H$-pyrazol-1-yl)propyl)-1$H$-tetrazol-5-amine, and the two compounds were excellent insensitive and moderate powerful. In addition, they synthesized 5-((3,4,5-trinitro-1$H$-pyrazol-1-yl)methyl)-1$H$-tetrazole by $N$-methylene-$C$ bridging TNP and tetrazole, which showed outstanding detonation properties and moderate insensitivity [113].
3. Nitrated-Bispyrazoles Based Compounds

Nitropyrazoles can be connected with nitrogen-rich heterocycles to obtain amazing energetic materials. In the previous section, nitropyrazoles bearing some polynitrogen heterocycles have been shown. Generally, these compounds exhibit some special properties, such as high detonation properties, good thermal stability, excellent safety, high density, and heat of formation, etc. Nitrated bispyrazoles also have attracted more and more attention, we will review the nitrated bispyrazole-based energetic materials in this section.

3.1. Directly Bridged Bis(Nitropyrazole)s

In 2014, Li et al. [27] synthesized several polynitro-substituted 1,4′-bridged-bispyrazoles energetic salts (64–67) as shown in Figure 25. They found that these compounds showed remarkable and unprecedented comprehensive properties (Table 12), and most of them with low toxicity were not hygroscopic. These compounds exhibited excellent impact sensitivities close to TATB, and the melting points and thermal decomposition temperatures were high, which could be applied as heat-resistant explosive. Compound 64 showed high $T_d$ approximating that of hexanitrostilbene (HNS, 316 °C). The energetic properties of compounds 64, 65, 65a, 66, and 67 were comparable with or superior to RDX, especially compound 66. In 2017, Tang et al. [114] prepared 4,4′,5,5′-tetranitro-2H,2′H-3,3′-bipyrazole (69) and its di-N-amino product (70), and the detailed route is described in Figure 26. Compound 70 showed good thermal stability and insensitivities as well as high detonation properties (Table 12). In addition, they synthesized 4,4′-dinitro-5,5′-diamino-2H,2′H-(3,3′-bipyrazole) (consisting of two 3-amino-4-nitropyrazole rings), this compound also show outstanding balance between thermal stability and safety (Table 12) [115]. Afterwards his team reported a variety of energetic materials based on compound 69 shown in Figure 27. Compounds 71, 73b, and 73h had high densities and good detonation velocities (Table 12), which were superior to RDX suggesting their use in secondary explosives. The dipotassium salt 73b had a high density of 2.029 g·cm$^{-3}$ and excellent thermal stability of 323 °C, and could be applied as primary explosives [116]. However, the poor impact sensitivity might restrict their further application. In 2019, Domasevitch and co-authors [117] found an efficient approach towards facile accumulation of nitro functionalities at the pyrazole platform. Compounds 74, 75, and 76 were synthesized according to Figure 28. From Table 12, the three compounds owned high decomposition temperatures above 290 °C, especially for 75 and 76. The introduction of three and four -NO$_2$ into the 4,4-bipyrazole scaffold could produce insensitive and thermally stable energetic materials with ideal densities and good detonation properties.

Figure 25. Synthesis of compounds 64–67.
Table 12. Physicochemical and energetic properties of compounds 64–76. The data of compounds 64–67 are from reference [27], the data of compounds 70 are from reference [114], the data of compounds 71–73 are from reference [116], the data of compounds 74–76 are from reference [117].

| Entry | ρ/g cm\(^{-3}\) | D/km·s\(^{-1}\) | P/GPa | T\(_{mo}^\circ\)C | T\(_{d}^\circ\)C | HOF/kJ·mol\(^{-1}\) | IS/J | FS/N |
|-------|-----------------|-----------------|-------|-----------------|-----------------|-----------------|------|------|
| 64    | 1.96            | 8.72            | 36.0  | 269             | 308             | 185.4           | >40  | -    |
| 65    | 1.89            | 8.60            | 35.0  | dec             | 242             | 388.1           | >40  | -    |
| 65a   | 1.88            | 8.62            | 34.6  | dec             | 262             | 274.7           | >40  | -    |
| 65b   | 1.73            | 8.04            | 27.3  | dec             | 228             | 246.5           | >40  | -    |
| 65c   | 1.67            | 8.09            | 27.1  | 249             | 272             | 506.4           | >40  | -    |
| 65d   | 1.71            | 8.20            | 27.9  | 210             | 272             | 448.8           | >40  | -    |
| 65e   | 1.72            | 8.34            | 29.0  | 212             | 266             | 558.0           | >40  | -    |
| 65f   | 1.75            | 8.33            | 31.1  | dec             | 259             | 331.2           | >40  | -    |
| 65g   | 1.82            | 8.45            | 31.0  | 247             | 297             | 557.0           | >40  | -    |
| 65h   | 1.72            | 8.23            | 28.9  | 166             | 261             | 700.4           | >40  | -    |
| 65i   | 1.80            | 8.54            | 32.8  | dec             | 260             | 428.1           | >40  | -    |
| 66    | 1.82            | 8.81            | 37.0  | 158             | 297             | 824.2           | 28   | -    |
| 67    | 1.87            | 8.65            | 35.1  | 260             | 284             | 477.9           | >40  | -    |
| 70    | 1.76            | 8.50            | 31.0  | -               | 252             | 475.7           | 30   | 360  |
| 71    | 1.88            | 8.99            | 36.0  | -               | 150             | 347.4           | 5    | 240  |
| 72    | 1.92            | 8.04            | 28.9  | 150             | 228             | -50.7           | 6    | 120  |
| 73a   | 2.03            | 7.77            | 27.3  | -               | 323             | -125.2          | 4    | 40   |
| 73b   | 1.85            | 8.85            | 35.8  | -               | 137             | 220.6           | 8    | 240  |
| 73c   | 1.77            | 8.67            | 31.5  | 94              | 155             | 220.9           | 10   | 240  |
| 73d   | 1.76            | 8.34            | 29.4  | -               | 193             | 116.2           | 10   | 240  |
| 73e   | 1.69            | 8.14            | 25.2  | -               | 196             | 353.3           | 15   | 360  |
| 73f   | 1.75            | 8.31            | 27.3  | 185             | 186             | 791.9           | 16   | 360  |
| 73g   | 1.76            | 8.22            | 26.5  | -               | 206             | 565.4           | 12   | 360  |
| 73h   | 1.81            | 8.95            | 34.2  | 187             | 193             | 1359.4          | 10   | 360  |
| 73i   | 1.80            | 8.54            | 28.9  | -               | 250             | 1269.7          | 18   | 360  |
| 74    | 1.79            | 7.53            | 22.1  | 377             | 382             | 203.5           | 30   | >360 |
| 75    | 1.81            | 8.36            | 28.6  | 306             | 314             | 224.9           | 20   | >360 |
| 76    | 1.86            | 8.52            | 31.1  | 292             | 298             | 227.8           | 4.5  | 192  |

Figure 25. Synthesis of compounds 64–67.

Figure 26. Synthesis of compounds 68–70.
was the most promising energetic material with high density, favorable thermal stability, and good performance; for example, the thermal decomposition temperature (311 °C) and detonation properties (27.9 GPa and 8.19 km·s⁻¹) of 77 were higher than those of TNT, and were comparable to those of TATB. By contrast, N,N'-ethylene bridged dinitraminobis(pyrazoles) and diazidobis(pyrazoles) owned better detonation performances, while having higher impact and friction sensitivity. Compound 80 was the most promising energetic material with high density, favorable thermal stability, and good detonation properties, which were comparable to RDX. In addition, the relatively low impact and friction sensitivities of 80 showed good integrated properties, highlighting its potential application as a replacement of RDX. In 2016, Fischer et al. [123] synthesized three different bisnitropyrazole-based energetic materials by N,N'-methylene bridge (86–88), the detailed synthetic route is displayed in Scheme A of Figure 30. These energetic compounds could be used for different applications.

### Table 12.

| Entry | ρ/ g·cm⁻³ | D / GPa | T / °C | ΔHOF / kJ·mol⁻¹ | H / °C | T / °C | St / g |
|-------|----------|-------|---|---------------|-----|---|-----|
| 65a   | 1.72     | 8.20  | 27.9| 32.8          | dec | 210 | 272 |
| 65b   | 1.75     | 8.33  | 31.1| dec           | 259 | 331.2| >40  |
| 65c   | 1.72     | 8.34  | 29.0| 212           | 266 | 558.0| >40  |
| 65d   | 1.71     | 8.20  | 27.9| 210           | 272 | 448.8| >40  |
| 65e   | 1.67     | 8.09  | 27.1| 249           | 272 | 506.4| >40  |
| 65f   | 1.73     | 8.04  | 27.3| dec           | 228 | 246.5| >40  |
| 65g   | 1.82     | 8.45  | 31.0| 247           | 297 | 557.0| >40  |
| 65h   | 1.72     | 8.33  | 31.1| dec           | 259 | 331.2| >40  |
| 65i   | 1.82     | 8.65  | 35.1| 260           | 284 | 477.9| >40  |
| 65j   | 1.76     | 8.50  | 31.0| 252           | 475.7| 30 | 360 |
| 65k   | 1.87     | 8.65  | 35.1| 260           | 284 | 477.9| >40  |

3.2. Alkyl-Bridged Bis(Nitropyrazoles)

Alkyl is also a good linkage to construct nitrogen-rich moieties, and many N,N'-alkyl-bridged energetic materials have been developed [112,118–121]. Yin et al. [122] developed a novel class of N,N'-ethylene-bridged bis(nitropyrazoles) with the synthetic route shown in Figure 29. Compounds 77–85 displayed various properties (Table 13) owing to the diversified functionalizations. Diaminobis(pyrazoles) showed good thermal stability, highly insensitivity, and favorable energetic performance; for example, the thermal decomposition temperature (311 °C) and detonation properties (27.9 GPa and 8.19 km·s⁻¹) of 77 were higher than those of TNT, and were comparable to those of TATB. By contrast, N,N'-ethylene bridged dinitraminobis(pyrazoles) and diazidobis(pyrazoles) owned better detonation performances, while having higher impact and friction sensitivity. Compound 80 was the most promising energetic material with high density, favorable thermal stability, and good detonation properties, which were comparable to RDX. In addition, the relatively low impact and friction sensitivities of 80 showed good integrated properties, highlighting its potential application as a replacement of RDX. In 2016, Fischer et al. [123] synthesized three different bisnitropyrazole-based energetic materials by N,N'-methylene bridge (86–88), the detailed synthetic route is displayed in Scheme A of Figure 30. These energetic compounds could be used for different applications.
according to their properties (Table 13), compound 86 was a secondary explosive with a high $T_d$ ($310 \, ^\circ C$), enhanced detonation parameters by contrast with HNS, and high sensitivity to external stimuli. Compound 87 exhibited excellent detonation velocity (approximately to CL-20). The higher performance and better thermal stability of 88 was relative to DDNP making it a potential candidate as a green primary explosive. In addition, the synthetic routes are economical. Afterwards, their group used a similar route to prepare bis(3,4-dinitro-1H-pyrazol-1-yl)methane (89) and bis(3,5-dinitro-1H-pyrazol-1-yl)methane (90) with high decomposition temperature and low sensitivities having capability as future energetic materials (Table 13) [94]. Gozin et al. [124] explored the possible influence factor of the thermostable property of explosives, and under the guidelines they proposed, they synthesized the compounds 91 and 92 with excellent thermal stability and moderate sensitivities shown in Figure 31 and Table 13.

![Synthesis of bis(nitropyrazoles) linked by $N,N'$-ethylene-bridge 77–85.](image)

Figure 29. Synthesis of bis(nitropyrazoles) linked by $N,N'$-ethylene-bridge 77–85.

Table 13. Physicochemical and energetic properties of 74–87. The data of compounds 77–85 are from reference [122], the data of compounds 86–88, CL-20 and DDNP are from reference [123], the data of compounds 89–90 are from reference [94], the data of compounds 91–92 are from reference [124].

| Entry | $\rho$/g cm$^{-3}$ | $D$/km s$^{-1}$ | $P$/GPa | OR/% | $T_d$/°C | HOF/[kJ mol$^{-1}$] | IS/J | FS/N |
|-------|------------------|----------------|--------|------|----------|------------------|------|------|
| 77    | 1.77             | 8.19           | 27.9   | -17.2| 311      | 218.9            | >40  | >360 |
| 78    | 1.84             | 8.75           | 34.3   | 3.5  | 80       | 380.6            | 7    | 80   |
| 79    | 1.72             | 7.80           | 24.2   | -19.0| 247      | 441.9            | 20   | 80   |
| 80    | 1.84             | 8.76           | 34.1   | 7.4  | 250      | 306.9            | 25   | 160  |
| 81    | 1.78             | 8.80           | 33.4   | -7.5 | 112      | 1233.9           | 4    | 60   |
| 82    | 1.88             | 7.88           | 27.0   | -7.8 | 319      | 230.0            | >40  | >360 |
| 83    | 1.76             | 8.56           | 31.0   | -7.5 | 135      | 1013.9           | 3    | 60   |
| 84    | 1.75             | 8.13           | 27.3   | -17.2| 256      | 237.9            | >40  | >360 |
| 85    | 1.83             | 8.71           | 33.7   | 3.5  | 81       | 368.1            | 6    | 60   |
| 86    | 1.80             | 8.33           | 29.6   | -40.2| 310      | 205              | 11   | >360 |
| 87    | 1.93             | 9.30           | 39.1   | -11.5| 205      | 379              | 4    | 144  |
| 88    | 1.73             | 8.02           | 26.0   | -44.7| 226      | 497              | 1.5  | 40   |
| 89    | 1.76             | 8.14           | 28.0   | -39.0| 319      | 302              | 25   | 360  |
| 90    | 1.72             | 7.97           | 26.3   | -39.0| 330      | 266              | 35   | 360  |
| 91    | 1.81             | 8.23           | 28.6   | -39.0| 262      | 224.2            | 14   | 352  |
| 92    | 1.81             | 8.36           | 29.7   | -51.4| 351      | 184.3            | 10   | 352  |
| CL-20 | 2.04             | 9.67           | 44.9   | -11.0| 195      | 365              | 3    | 96   |
| DDNP  | 1.72             | 76.5           | 23.8   | -60.9| 157      | 139              | 1    | 5    |
with the conventional heat resistant explosive HNS, shown in Figure 34. This compound exhibited an excellent decomposition temperature (341 °C) and good insensitivity (IS > 40 J, FS > 360 N) as well as high detonation properties (8.69–8.74 km·s⁻¹ of D and 33.4–34.0 GPa of P). Moreover, Li et al. [124] synthesized the compound 106 with the procedure shown in Figure 34. This compound exhibited an excellent decomposition temperature (341 °C), high calculated detonation velocity of 8.52 km·s⁻¹, and detonation pressure of 30.6 GPa. It also showed impressive insensitivities (IS = 22 J, FS = 352, and ESD = 1.05 J). These showed building ring bridged bis(nitropyrazoles) can be an effective approach to enhance the properties of energetic materials.

Figure 29. Synthesis of bis(nitropyrazoles) linked by N,N’-methylene-bridge 86–90.

Figure 30. Synthesis of bis(nitropyrazoles) linked by N,N’-ethylene-bridge 88–94.

Figure 31. Synthesis of compounds 91 and 92.

Figure 32. Synthesis of compound 93.

3.3. Ring-Bridged Bis(Nitropyrazoles)

Ring-bridge is an important connector linking bis(nitropyrazoles) to obtain high performance energetic materials. Pagoria et al. [125] reported the trimerization of LLM-116. 4-Diazo-3,5-bis(4-aminodinitropyrazol-1-yl) pyrazole (95) containing a stable diazo group was synthesized, and the detailed route is shown in Figure 32. Compound 93 was more thermally stable (278 °C of Td) than LLM-116, attributing to the considerable hydrogen bonding between -NH₂ and -NO₂, and the short contact between the =N₂ and -NO₂ through the intermolecular interactions. Moreover, it was insensitive to impact, friction, and spark. Yan et al. [126] designed mono and bi(1,2,4-oxadiazole) rings to bridge polynitropyrazoles (Figure 33). Among compounds 94–99, 98, and 99 owned the highest detonation velocity of 8.90 and 8.87 km·s⁻¹, detonation pressure of 35.1 and 34.5 GPa, respectively. 94 and 95 processed good stability (272–274 °C) and good insensitivity (IS > 30 J and FS > 360 N) as well as high detonation properties (8.69–8.74 km·s⁻¹ of D and 33.4–34.0 GPa of P). 96 and 97 had the high thermal stability over 310 °C and good sensitivity (IS > 40 J, FS > 360 N). Comparing with the conventional heat resistant explosive HNS, 96 and 97 owned better detonation properties (7.99–8.03 km·s⁻¹ of D, 25.2–26.4 GPa of P). Also, their team used the similar routes to synthesize the bis(nitropyrazoles) with 1,3,4-oxadiazole (100–105) [127]. The properties of these compounds are showed in Table 14. Moreover, Li et al. [124] synthesized the compound 106 with the procedure shown in Figure 34. This compound exhibited an excellent decomposition temperature (341 °C), high calculated detonation velocity of 8.52 km·s⁻¹, and detonation pressure of 30.6 GPa. It also showed impressive insensitivities (IS = 22 J, FS = 352, and ESD = 1.05 J). These showed building ring bridged bis(nitropyrazoles) can be an effective approach to enhance the properties of energetic materials.
In addition, there are some other fused ring-bridged bis(nitropyrazoles). In 2017, Yin and co-authors [128] synthesized compound 109 and its derivatives according to the procedure shown in Figure 35, and their physicochemical and energetic properties are shown in Table 15. Among these compounds, 107a had a high density and decomposition temperature as well as the good safety parameters. The introduction of nitramino group gave 110 and 111 highest detonation velocities and pressures, while they also exhibited sensitive properties to mechanical stimuli. Considering the whole aspect, 108a was featured with promising integrated energetic performance exceeding those of the benchmark explosive RDX. Shreeve’s group prepared (112) obtained from compound 69 by N-azo coupling reactions shown in Scheme A of Figure 36 [114]. Compound 112 had a high density of 1.955 g·cm\(^{-3}\) and a good thermal stability (233 °C). Its detonation properties (9.63 km·s\(^{-1}\) and 44.0 GPa) were comparable to CL-20, much better than those of RDX and HMX. In addition, the IS of 10 J and FS of 240 N showed it was more stable than CL-20. These indicated compound 112 was a superior
energetic explosive. In 2018, her team developed an efficient synthetic method of ring closure of polynitropyrazoles with \(N,N'\)-ethylene/propylene bridges (Figure 36, Scheme B). Compounds 113 and 114 showed excellent thermal stability (261 °C for 113, 280 °C for 114), good detonation properties and moderate insensitivities, making them potential candidates as HEDMs. This ring closure strategy could provide new ideas of designing thermally stable explosives.

![Figure 34. Synthesis of compound 106.](image)

![Figure 35. Synthesis of compounds 107a–111.](image)

| Entry | \(\rho/g\cdot cm^{-3}\) | \(D/km\cdot s^{-1}\) | \(P/GPa\) | \(T_d/°C\) | \(\text{HOF}/kJ\cdot g^{-1}\) | IS/J | FS/N |
|-------|-----------------|-----------------|----------|---------|-----------------|-------|------|
| 107a  | 1.90            | 8.79            | 34.3     | 261     | 1.10            | 15    | 240  |
| 107b  | 1.82            | 8.52            | 31.7     | 220     | 0.97            | 40    | 360  |
| 108a  | 1.86            | 8.89            | 35.9     | 221     | 1.05            | 35    | 360  |
| 108b  | 1.83            | 8.69            | 33.2     | 207     | 1.33            | 25    | 360  |
| 109   | 1.79            | 8.36            | 29.6     | 242     | 0.96            | 15    | 160  |
| 110   | 1.94            | 9.23            | 38.8     | 117     | 1.30            | 3     | 20   |
| 111   | 1.87            | 9.03            | 37.1     | 138     | 1.32            | 10    | 80   |
In general, the physical and energetic properties of bridged bis(nitropyrazole)s can be adjusted by the bridged groups. The design of novel bridged group would be a key factor to synthesize new HEDMs, and forming polycyclic derivatives even cage compounds could be more attractive. In addition, the salts of bridged bis(nitropyrazole)s should be explored in-depth.
4. Nitrat moved Pyrazolo[4,3-c]Pyrazoles and Their Derivatives

Application of molecular design and explosive performance prediction has explored many novel energetic materials based on pyrazolopyrazole ring system \([2,132,133]\). Heterocycles like pyrazolo-pyrazole always own high density and oxygen balance, good thermal stability, and enhanced energetic performance of an energetic material.

3,6-Dinitropyrazolo[4,3-c]pyrazole (DNPP) is a new type of energetic material with attractive properties (1.865 g·cm\(^{-1}\) of \(\rho\), 42.42% of nitrogen content, 273 kJ·mol\(^{-1}\), 330.8 °C of \(T_d\) and 68 cm of \(D_{50}\)). This compound synthesized from 3,5-dimethylpyrazole was firstly reported by Dalinger and co-workers \([134]\). Pagoria et al. \([135]\) improved the synthetic route to DNPP as shown in Scheme A of Figure 38. In this procedure, 4-diazo-3,5-dimethylpyrazole salt is an important intermediate. Li et al. \([136]\) improved the process of 4-diazo-3,5-dimethylpyrazole salt using freezing crystallization instead of extraction which avoided large use of organic solvents and improved its yield. This procedure has several advantages, such as ease of synthesis scale-up and better product yield. In addition, Luo et al. \([137]\) proposed that DNPP could be obtained by dehydration condensation, primary nitration, reduction, diazotization, cyclization, secondary nitration, oxidation, and decarboxylation nitration with acetylacetone and hydrazine hydrate as raw materials (Figure 38, Scheme B).

Due to the active N-H bond in molecule of DNPP, it is easy to obtain its energetic salts. In 2014, Zhang et al. \([138]\) reported a series of nitrogen-rich energetic salts based on the anion of DNPP (123a–m) shown in Figure 39. Salts 123a–e could be obtained by reacting DNPP with ammonia, hydrazine, hydroxylamine, 3,5-diamino-1,2,4-triazole, and 3,4,5-triamino-1,2,4-triazole. Salts 123f–j could be synthesized by reacting Na\(_2\)DNPP with guanidine nitrate, aminoguanidine, diaminoguanidine, triaminoguanidinium, and 2-iminium-5-nitrinooctahydroimidazo [4,5-d]imidazole hydrochlorides.
Salts 123k–m were acquired by the reaction of DNPP with NaOH, KOH and AgNO₃ respectively. Table 17 displays the properties of these energetic salts. It was notable that the ammonium salt (123a), hydroxylammonium salt (123b) and guanidinium salt (123f) exhibited outstanding decomposition temperatures of >300 °C. Furthermore, the sodium salt (123k) and potassium (123l) salt of DNPP were thermally stable up to 395 °C and 365 °C, respectively. In addition, most of the salts showed high calculated detonation properties, especially 123b owned the highest detonation velocity and pressure. Considering the balance of safety and energetic properties as well as physical properties, 123b could be a competitive candidate in insensitive HEDMs. Luo and co-authors synthesized the basic lead salt of DNPP (Pb-DNPP) and the 3,6-dihydrazine-1,2,4,5-tetrazine salt of DNPP (DHT-DNPP), and studied their thermal decomposition behaviors. Like 123k–m, the introduction of heavy cations made the salts higher densities and $T_d$. Combining other organic amines salts of DNPP [139], these salts showed good thermal stabilities.

![Figure 38. Synthesis of DNPP.](image1)

![Figure 39. Synthesis of salts of DNPP.](image2)
Table 17. Properties of energetic compounds 123a–m. The data of compounds 123a–123m are from reference [138].

| Entry | $\rho$/g·cm$^{-3}$ | $D$/km·s$^{-1}$ | $P$/GPa | $T_d$/$^\circ$C | HOF/kJ·mol$^{-1}$ | IS/J | FS/N | OB/% |
|-------|------------------|-----------------|----------|-----------------|-----------------|------|------|------|
| 123a  | 1.69             | 8.21            | 25.4     | 328             | 158.5           | >40  | 360  | −27  |
| 123b  | 1.82             | 9.01            | 35.4     | 327             | 274.2           | 29   | 360  | −12  |
| 123c  | 1.72             | 8.86            | 30.3     | 247             | 501.0           | 16   | 160  | −30  |
| 123d  | 1.71             | 8.04            | 24.5     | 287             | 481.9           | >40  | 360  | −30  |
| 123e  | 1.67             | 8.23            | 24.6     | 289             | 963.8           | >40  | 360  | −41  |
| 123f  | 1.68             | 7.95            | 22.5     | 324             | 173.3           | >40  | 360  | −40  |
| 123g  | 1.69             | 8.40            | 25.6     | 222             | 477.0           | >40  | 360  | −41  |
| 123h  | 1.71             | 8.73            | 28.0     | 209             | 679.6           | >40  | 360  | −42  |
| 123i  | 1.76             | 8.81            | 29.9     | 215             | 605.5           | 12   | 80   | −31  |
| 123j  | 1.79             | 8.36            | 27.9     | 238             | 505.6           | 23   | 160  | −27  |
| 123k  | 2.14             | -               | -        | -               | -               | -    | -    | 0    |
| 123l  | 2.20             | -               | -        | -               | -               | -    | -    | 0    |
| 123m  | 3.27             | -               | -        | -               | -               | -    | -    | 0    |

In addition, 1,4-Diamino-3,6-dinitropyrazolo[4,3-c]pyrazole (LLM-119) is a derivative of DNPP with a predicted energy of 104% HMX and good insensitivity to friction and electric spark stimulation [2]. It is also a very important intermediate of synthesizing novel high-performance energetic materials. Li et al. [140] used NaOH and H$_2$NOSO$_3$H to realize the N-amination of DNPP, while the yield was low (10.4%). Yin reported a modified procedure using 1,8-diazabicycloundec-7-ene (DBU) and O-tosylhydroxylamine (TsONH$_2$) as organic solvents with a good yield [141]. He also developed a series of DNPP derivatives based on N-functionalization strategy including several ionic salts of DNPP, the synthesis route is displayed in Figure 40 (Scheme A). As shown in Table 18, compounds 125, 126 and 126c exhibited high densities and excellent detonation velocities and pressures, which were superior to the current secondary explosive benchmark HMX. These compounds except 126d and 126e were sensitive to stimulation, especially for 126i also showed excellent density and good thermal stability. These could make compound the potassium salt as a green primary explosive. Compounds 126a, 126b, 126c and 126g showed good possibilities for application in bipropellants owing to the high values of (N + O) content and specific impulse. Li and co-author [142] synthesized another four kinds of neutral explosives based on N-functionalization of DNPP shown in Scheme B of Figure 40. Comparing with LLM-119, compound 127 showed slightly lower energetic and physical properties due to the only one -NH$_2$. Compounds 130 owned the relatively high density, good thermal stability, outstanding detonation properties, and reasonable sensitivities, which could be a useful energetic material. Li et al. [143,144] also synthesized several salts of N-nitramino DNPP, which exhibited good energetic properties.

In addition, Zhang et al. [145] introduced the dinitromethyl group and fluorodinitromethyl group into DNPP molecule and synthesized five fused-ring energetic derivatives (131–132) shown in Figure 41. Among these compounds, the dipotassium salt (131a) was formed as an interesting three-dimensional metal-organic framework (MOF) and exhibited outstanding detonation performances (9.02 km·s$^{-1}$ of $D$ and 33.6 GPa of $P$), which were comparable to that of Pd(N$_3$)$_2$. The compound 132 had a high density of 1.939 g·cm$^{-3}$, high decomposition temperature of 213 $^\circ$C and desired mechanical sensitivities (IS: 12 J; FS: 240 N), which could be a competitive candidate of RDX. These energetic compounds containing dinitromethyl or fluorodinitromethyl group enrich the energetic compound library of pyrazolo[4,3-c]pyrazoles. Furthermore, their group incorporated two tetryazole groups into DNPP molecule, and synthesized 3,6-dinitro-1,4-di(1H-tetrazol-5-yl)-pyrazolo[4,3-c]pyrazole (133) and its ionic derivatives (133a–f) shown in Figure 42 [146]. The physicochemical and energetic properties of these compounds are shown in Table 19. These compounds were thermally stable and insensitive to mechanical stimulation. The potassium salt (133a) possessed a high thermal decomposition temperature (329 $^\circ$C of $T_d$) and low sensitivities (IS: 25 J; FS: 252 N). In contrast with other derivatives from DNPP, compound 133f owned the best mechanical sensitivities (IS: >60 J; FS: >360 N). Compounds 133, 133a,
and 133d possessed good comprehensive properties, including remarkable thermal decomposition temperatures, excellent insensitivity, and favorable detonation performance.

In addition, 1,4-Diamino-3,6-dinitropyrazolo[4,3-c]pyrazole (LLM-119) is a derivative of DNPP with a predicted energy of 104% HMX and good insensitivity to friction and electric spark stimulation [2]. It is also a very important intermediate of synthesizing novel high-performance energetic materials. Li et al. [140] used NaOH and H₂NOSO₃H to realize the N-amination of DNPP, while the yield was low (10.4%). Yin reported a modified procedure using 1,8-diazabicycloundec-7-ene (DBU) and O-tosylhydroxylamine (TsONH₂) as organic solvents with a good yield [141]. He also developed a series of DNPP derivatives based on N-functionalization strategy including several ionic salts of DNPP, the synthesis route is displayed in Figure 40 (Scheme A). As shown in Table 18, compounds 125, 126 and 126c exhibited high densities and excellent detonation velocities and pressures, which were superior to the current secondary explosive benchmark HMX. These compounds except 126d and 126e were sensitive to stimulation, especially for 126i also showed excellent density and good thermal stability. These could make compound the potassium salt as a green primary explosive. Compounds 126a, 126b, 126c and 126g showed good possibilities for application in bipropellants owing to the high values of (N + O) content and specific impulse. Li and co-author [142] synthesized another four kinds of neutral explosives based on N-functionalization of DNPP shown in Scheme B of Figure 40. Comparing with LLM-119, compound 127 showed slightly lower energetic and physical properties due to the only one -NH₂. Compounds 130 owned the relatively high density, good thermal stability, outstanding detonation properties, and reasonable sensitivities, which could be a useful energetic material. Li et al. [143,144] also synthesized several salts of N-nitramino DNPP, which exhibited good energetic properties.

Figure 40. Synthesis of N-functional derivatives of DNPP.

Table 18. Physical and detonation properties of energetic compounds LLM-119 and 124–130. The data of compounds LLM-119 and 124–126i are from reference [141], the data of compounds 127–130 are from reference [142].

| Entry   | ρ (g cm⁻³) | D (km s⁻¹) | P (GPa) | Tₐ (°C) | HOF (kJ mol⁻¹) | IS (J) | FS (N) | OBJ (%) | N + O (%) | Iₛ/p (s) |
|---------|------------|------------|---------|---------|---------------|--------|--------|---------|-----------|---------|
| LLM-119 | 1.84       | 8.86       | 33.9    | 230     | 467.0         | 15     | 160    | -14.0   | 77.2      | 246     |
| 124     | 1.82       | 8.67       | 33.1    | 206     | 133.7         | 10     | 120    | 9.2     | 78.2      | 245     |
| 125     | 1.96       | 9.46       | 40.9    | 145     | 550.9         | 3      | 20     | 22.2    | 83.3      | 269     |
| 126     | 1.93       | 9.51       | 41.8    | 128     | 595.2         | 2      | 20     | 15.1    | 84.3      | 274     |
| 126a    | 1.81       | 8.98       | 35.9    | 181     | 423.1         | 10     | 120    | 0       | 84.1      | 270     |
| 126b    | 1.85       | 9.40       | 39.5    | 174     | 738.9         | 5      | 60     | -4.2    | 84.8      | 280     |
| 126c    | 1.88       | 9.50       | 41.3    | 170     | 531.2         | 7      | 120    | 8.3     | 85.4      | 282     |
| 126d    | 1.68       | 8.30       | 26.9    | 190     | 454.7         | 35     | 360    | -14.7   | 80.7      | 239     |
| 126e    | 1.71       | 8.61       | 29.3    | 153     | 692.9         | 30     | 360    | -17.2   | 81.5      | 247     |
| 126f    | 1.70       | 8.88       | 30.8    | 141     | 1144.8        | 10     | 80     | -21.3   | 82.8      | 258     |
| 126g    | 1.78       | 9.17       | 36.0    | 163     | 1683.3        | 5      | 60     | -9.3    | 84.2      | 280     |
| 126h    | 1.83       | 9.00       | 33.1    | 203     | 1599.5        | 10     | 120    | -23.0   | 78.6      | 244     |
| 126i    | 2.11       | 8.31       | 31.2    | 208     | 152.9         | 2      | 20     | 16.2    | 68.0      | 226     |
| 127     | 1.74       | 7.93       | 27.9    | 178     | 356.0         | 14     | 280    | -41.3   | 76.0      | -       |
| 128     | 1.83       | 8.48       | 32.8    | 208     | 18.8          | 12     | 160    | -18.4   | 78.2      | -       |
| 129     | 1.74       | 7.82       | 27.1    | 198     | 863.0         | 10     | 240    | -51.9   | 75.3      | -       |
| 130     | 1.90       | 8.84       | 36.5    | 296     | 269.0         | 16     | 300    | -20.9   | 78.2      | -       |
properties, further functionalization of these compounds could be interesting. However, the synthesis of DNPP are still multistep reactions with unsatisfactory yield. The more efficient and facile technology should be investigated.

In recent years, a lot of scholars over the world have paid much attention to the development of nitrogen-rich heterocyclic energetic materials, due to their high positive heat of formation, low sensitivity, tailored thermal stability, and attractive detonation performance. According to the reference [37], a new energetic compound should be environmentally friendly, easy and economical to synthesize, thermal stable (Td > 200 °C), insensitive to mechanical stimulation (IS > 7 J; FS > 120 N), good detonation

| Entry | ρ/g cm⁻³ | D/km·s⁻¹ | P/GPa | T_d/°C | HOF/kJ·mol⁻¹ | IS/J | FS/N |
|-------|----------|----------|-------|--------|--------------|------|------|
| 133   | 1.79     | 8.72     | 30.9  | 281    | 1111.5       | 15   | 192  |
| 133a  | 2.00     | 8.81     | 28.5  | 329    | 638.9        | 25   | 252  |
| 133b  | 1.69     | 8.40     | 26.2  | 280    | 916.8        | 19   | >360 |
| 133c  | 1.61     | 8.24     | 26.0  | 178    | 1062.2       | 27.5 | 324  |
| 133d  | 1.75     | 9.08     | 31.3  | 221    | 1223.0       | 12   | 144  |
| 133e  | 1.62     | 8.02     | 22.4  | 299    | 926.9        | >60  | >360 |
| 133f  | 1.64     | 8.40     | 24.9  | 255    | 1143.3       | 35   | >360 |

Nitratied pyrazolo[4,3-c]pyrazoles own acceptable performances both the energetic and physical properties, further functionalization of these compounds could be interesting. However, the synthesis of DNPP are still multistep reactions with unsatisfactory yield. The more efficient and facile synthesis technology should be investigated.

5. Conclusions

In recent years, a lot of scholars over the world have paid much attention to the development of nitrogen-rich heterocyclic energetic materials, due to their high positive heat of formation, low sensitivity, tailored thermal stability, and attractive detonation performance. According to the reference [37], a new energetic compound should be environmentally friendly, easy and economical to synthesize, thermal stable (T_d > 200 °C), insensitive to mechanical stimulation (IS > 7 J; FS > 120 N), good detonation
properties ($D > 8.5 \text{ km} \cdot \text{s}^{-1}$), and not insoluble in water. For the nitropyrazoles-based energetic materials, most of them can meet these requirements. Some nitropyrazole-based compounds show good performance as castable explosives, such as compounds 1, 2, 3, 5, 3,4-DNP, 46, 48, 53, 54, and MTNP, which are competitive candidates of TNT. Some exhibited excellent thermal stability such as compounds 17, 28, 37, 64, 75, 86, 90, 92, 101, 120, DNPP, etc. Further, many showed a balance between good safety and high detonation performance. The introduction of high-nitrogen groups (including fused-ring, polynitramino group, polynitromethyl group, etc) to nitropyrazoles can be useful approach for the further development of new-generation HEDMs. In addition, the concept of forming ionic salts, bridged structures and pyrazolo-pyrazoles provides novel insights to synthesize high performance energetic materials. It is better to synthesize new energetic compounds under the direction of theoretical calculation, so it is important to understand the relationship between structures and properties for the design and synthesis of new nitropyrazoles-based energetic materials.

Furthermore, there are some areas requiring improvement for the further synthesis of novel nitropyrazoles-based EMs. First, traditional nitration is generally used in the synthesis of nitropyrazoles-based EMs, which does not meet the requirements of modern green chemistry. It is vital to find out the suitable green nitrating agents and catalysts in the future synthesis process. Second, many syntheses of nitropyrazoles-based EMs entail several steps, leading to a low yield and high cost. Therefore, it is necessary to search for an efficient route when preparing new HEDMs.

Author Contributions: Conceptualization, S.Z.; writing—original draft preparation, S.Z. and Q.J.; writing—review and editing, S.Z. and Z.G.; data curation, N.L. and D.L.; supervision, K.K.; project administration, K.K. and J.Z.; funding acquisition, K.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China, grant numbers 21673182 and 21703168.

Caution: Readers are reminded that the information given in this review is intended to cover the progress of recent research on energetic azo materials. Most of the molecules collected in this review are energetic materials that may be explosive under certain conditions. Their syntheses should be carried out by experienced personnel and handled with caution. In any case, carefully planned safety protocols and proper protective equipment, such as Kevlar gloves, ear protection, safety shoes and plastic spatulas, should be utilized at all times, especially when working on a large scale (>1 g). The authors strongly suggest that the original references be consulted for detailed safety information.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Becuwe, A.; Delclos, A. Low-sensitivity explosive compounds for low vulnerability warheads. Propell. Explos. Pyrot. 1993, 18, 1–10. [CrossRef]
2. Pagoria, P.F.; Lee, G.S.; Mitchell, A.R.; Schmidt, R.D. A review of energetic materials synthesis. Thermochim. Acta 2002, 384, 187–204. [CrossRef]
3. Guo, J.; Cao, D.; Wang, J.; Wang, Y.; Qiao, R.; Li, Y. Review on synthesis of nitropyrazoles. Chin. J. Energ. Mater. 2014, 22, 872–879.
4. Talawar, M.B.; Sivabalan, R.; Mukundan, T.; Muthurajan, H.; Sikder, A.K.; Gandhe, B.R.; Rao, A.S. Environmentally compatible next generation green energetic materials (GEMs). J. Hazard. Mater. 2009, 161, 589–607. [CrossRef]
5. Tsisyhevsky, R.V.; Sharia, O.; Kuklja, M.M. Molecular theory of detonation initiation: Insight from first principles modeling of the decomposition mechanisms of organic nitro energetic materials. Molecules 2016, 21, 236. [CrossRef]
6. Yan, Q.-L.; Cohen, A.; Petrutik, N.; Shlomovich, A.; Zhang, J.-G.; Gozin, M. Formation of highly thermostable copper-containing energetic coordination polymers based on oxidized triaminoguanidine. ACS Appl. Mater. Inter. 2016, 8, 21674–21682. [CrossRef]
7. Yan, Q.-L.; Gozin, M.; Zhao, F.-Q.; Cohen, A.; Pang, S.-P. Highly energetic compositions based on functionalized carbon nanomaterials. Nanoscale 2016, 8, 4799–4851. [CrossRef]
8. Chen, X.; Zhang, C.; Bai, Y.; Guo, Z.; Yao, Y.; Song, J.; Ma, H. Synthesis, crystal structure and thermal properties of an unsymmetrical 1, 2, 4, 5-tetrazine energetic derivative. Acta Crystallogr. C 2018, 74, 666–672. [CrossRef]

9. Klapötke, T.M. High Energy Density Materials; Springer: Berlin, Germany, 2007; Volume 125.

10. An, C.W.; Li, F.S.; Song, X.L.; Wang, Y.; Guo, X.D. Surface Coating of RDX with a Composite of TNT and an Energetic-Polymer and its Safety Investigation. Propell. Explos. Pyrot. 2009, 34, 400–405. [CrossRef]

11. Jia, Q.; Kou, K.-C.; Zhang, J.-Q.; Zhang, S.-J.; Xu, Y.-L. Study on the dissolution behaviors of CL-20/TNT co-crystal in N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). J. Therm. Anal. Calorim. 2018, 134, 2375–2382. [CrossRef]

12. Simpson, R.L.; Urtiew, P.A.; Ornellas, D.L.; Moody, G.L.; Scribner, K.J.; Hoffman, D.M. CL-20 Performance Exceeds that of HMX and its Sensitivity is Moderate. Propell. Explos. Pyrot. 1997, 22, 249–255. [CrossRef]

13. Wang, Y.; Jiang, W.; Song, X.; Deng, G.; Li, F. Insensitive HMX (octahydro-1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazocine) nanocrystals fabricated by high-yield, low-cost mechanical milling. Cent. Eur. J. Energ. Mater. 2013, 10, 277–287.

14. Qiu, H.; Stepanov, V.; Di Stasio, A.R.; Chou, T.; Lee, W.Y. RDX-based nanocomposite microparticles for significantly reduced shock sensitivity. J. Hazard. Mater. 2011, 185, 489–493. [CrossRef] [PubMed]

15. Kolb, J.R.; Rizzo, H.F. Growth of 1, 3, 5-Triamino-2, 4, 6-trinitrobenzene (TATB) I. Anisotropic thermal expansion. Propell. Explos. Pyrot. 1979, 4, 10–16. [CrossRef]

16. Nair, U.R.; Sivabalan, R.; Gore, G.M.; Geetha, M.; Asthana, S.N.; Singh, H. Hexanitrohexaazaisowurtzitane (CL-20) and CL-20-based formulations. Combust. Explo. Shock Waves 2005, 41, 121–132. [CrossRef]

17. Nair, U.R.; Asthana, S.N.; Rao, A.S.; Gandhe, B.R. Advances in high energy materials. Def. Sci. J. 2010, 60, 137. [CrossRef]

18. Swain, P.K.; Singh, H.; Tewari, S.P. Energetic ionic salts based on nitrogen-rich heterocycles: A prospective study. J. Mol. Liq. 2010, 151, 87–96. [CrossRef]

19. Gao, H.; Shreeve, J.M. Azole-based energetic salts. Chem. Rev. 2011, 111, 7377–7436. [CrossRef]

20. Kröber, H.; Teipel, U. Crystallization of insensitive HMX. Propell. Explos. Pyrot. 2008, 33, 33–36. [CrossRef]

21. Zhang, S.; Kou, K.; Zhang, J.; Jia, Q.; Xu, Y. Compact energetic crystals@ urea-formaldehyde resin micro-composites with evident insensitivity. Compos. Commun. 2019, 15, 103–107. [CrossRef]

22. Zhang, S.; Gao, Z.; Jia, Q.; Liu, N.; Zhang, J.; Kou, K. Fabrication and characterization of surface modified HMX@ PANI core-shell composites with enhanced thermal properties and desensitization via in situ polymerization. Appl. Surf. Sci. 2020, 515, 146042. [CrossRef]

23. Liu, N.; Duan, B.; Lu, X.; Mo, H.; Xu, M.; Zhang, Q.; Wang, B. Preparation of CL-20/DNDAP cocrystals by a rapid and continuous spray drying method: An alternative to cocrystal formation. CrystEngComm 2018, 20, 2060–2067. [CrossRef]

24. Liu, N.; Duan, B.; Lu, X.; Zhang, Q.; Xu, M.; Mo, H.; Wang, B. Preparation of CL-20/TFAZ cocrystals under aqueous conditions: Balancing high performance and low sensitivity. CrystEngComm 2019, 21, 7271–7279. [CrossRef]

25. Zhang, S.; Zhang, J.; Kou, K.; Jia, Q.; Xu, Y.; Liu, N.; Hu, R. Standard Enthalpy of Formation, Thermal Behavior, and Specific Heat Capacity of 2HNIW- HMX Co-crystals. J. Chem. Eng. Data 2018, 64, 42–50. [CrossRef]

26. Bolter, M.F.; Harter, A.; Klapötke, T.M.; Stierstorfer, J. Isomers of Dinitropyrazoles: Synthesis, Comparison and Tuning of their Physicochemical Properties. Chempluchem 2018, 83, 804–811. [CrossRef]

27. Li, C.; Liang, L.; Wang, K.; Bian, C.; Zhang, J.; Zhou, Z. Polynitro-substituted bipyrazoles: A new family of high-performance energetic materials. J. Mater. Chem. A 2014, 2, 18097–18105. [CrossRef]

28. Liu, W.; Wang, J.; Cao, D.L.; Chen, L.; Liu, Y.; Zhao, X. Synthesis of 3,5-dinitropyrazole. Appl. Chem. Ind. 2018, 47, 30–34. [CrossRef]

29. Zhang, P.; Kumar, D.; Zhang, L.; Shem-Tov, D.; Petrutik, N.; Chinnam, A.K.; Yao, C.; Pang, S.; Goinz, M. Energetic Butterfly: Heat-Resistant Diaminodinitro trans-Bimane. Molecules 2019, 24, 4324. [CrossRef]

30. Göbel, M.; Klapötke, T.M. Development and testing of energetic materials: The concept of high densities based on the trinitroethyl functionality. Adv. Funct. Mater. 2009, 19, 347–365. [CrossRef]

31. Klapötke, T.M.; Sabaté, C.M. Nitrogen-rich tetrazolium azotetrazolates salts: A new family of insensitive energetic materials. Chem. Mater. 2008, 20, 1750–1763. [CrossRef]

32. Zhao, T.X.; Li, L.; Dong, Z.; Zhang, Y.; Zhang, G.Z.; Huang, M.; Li, H.B. Research Progress on the Synthesis of Energetic Nitroazoles. Chin. J. Org. Chem. 2014, 34, 304–315. [CrossRef]
33. Huang, A.; Wo, K.; Lee, S.Y.C.; Kneitschel, N.; Chang, J.; Zhu, K.; Mello, T.; Bancroft, L.; Norman, N.J.; Zheng, S.-L. Regioselective synthesis, NMR, and crystallographic analysis of N1-substituted pyrazoles. J. Org. Chem. 2017, 82, 8864–8872. [CrossRef] [PubMed]

34. Lahm, G.P.; Cordova, D.; Barry, J.D. New and selective ryanodine receptor activators for insect control. Bioorg. Med. Chem. 2009, 17, 4127–4133. [CrossRef] [PubMed]

35. Cavero, E.; Uriel, S.; Romero, P.; Serrano, J.L.; Giménez, R. Tetrahedral zinc complexes with liquid crystalline and luminescent properties: Interplay between nonconventional molecular shapes and supramolecular mesomorphism order. J. Am. Chem. Soc. 2007, 129, 11608–11618. [CrossRef]

36. Dalinger, I.L.; Vatsadse, I.A.; Shikinova, T.K.; Popova, G.P.; Ugrak, B.I.; Shevelev, S.A. Nitropyrazoles. Russ. Chem. Bull. 2010, 59, 1631–1638. [CrossRef]

37. Qu, Y.; Babailov, S.P. Azo-linked high-nitrogen energetic materials. J. Mater. Chem. A 2018, 6, 1915–1940. [CrossRef]

38. Janssen, J.; Koenders, H.J.; Kruse, C.G.; Habraken, C.L. Pyrazoles. XII. Preparation of 3-(5)-nitropyrazoles by thermal rearrangement of N,N'-substituted pyrazoles. J. Org. Chem. 1973, 38, 1777–1782. [CrossRef]

39. Habraken, C.L.; Janssen, J. Pyrazoles. VIII. Rearrangement of N-nitropyrazoles. Formation of 3-nitropyrazoles. J. Org. Chem. 1971, 36, 3081–3084. [CrossRef]

40. Verbruggen, R. Cycloaddition with 2-chloro-1-nitroethylene. Chimia 1975, 29, 350–352.

41. Li, C.; Sun, T.; Chen, X. Synthesis of 3-Nitropyrazole. Chin. J. Syn. Chem. 2012, 3081–3084. [CrossRef]

42. Li, H.; Xiong, B.; Jiang, J.; Zheng, X.; Li, Z.; Ma, Y. Synthesis and Characterization of 3-Nitropyrazole and its Salts. Chin. J. Energ. Mater. 2008, 31, 102–104.

43. Tian, X.; Li, J.; Wang, J. Synthesis of 3,4-Dinitropyrazole. Chin. J. Syn. Chem. 2012, 20, 117–118.

44. Zhao, X.X.; Zhang, J.C.; Li, S.H.; Yang, Q.P.; Li, Y.C.; Pang, S.P. A Green and Facile Approach for Synthesis of Nitro Heteroaromatics in Water. Org. Process Res. Dev. 2014, 18, 886–890. [CrossRef]

45. Katritzky, A.R.; Scriven, E.F.V.; Majumder, S.; Akhmedova, R.G.; Akhmedov, N.G.; Vakulenko, A.V. Direct nitration of five membered heterocycles. Arkivoc 2005, 3, 179–191.

46. Ravi, P.; Gore, G.M.; Tewari, S.P.; Sikder, A.K. A simple and environmentally benign nitration of pyrazoles by impregnated bismuth nitrate. J. Heterocyclic Chem. 2013, 50, 1322–1327. [CrossRef]

47. Yi, J.H.; Hu, S.Q.; Liu, S.N.; Cao, D.L.; Ren, J. Theoretical study on structures and detonation performances for nitro derivatives of pyrazole by density functional theory. Chin. J. Energy. Mater. 2010, 18, 252–256.

48. Rao, E.N.; Ravi, P.; Tewari, S.P.; Rao, S.V. Experimental and theoretical studies on the structure and vibrational properties of nitropyrazoles. J. Mol. Struct. 2013, 1043, 121–131.

49. Ravi, P. Experimental and DFT studies on the structure, infrared and Raman spectral properties of dinitropyrazoles. J. Mol. Struct. 2015, 1079, 433–447. [CrossRef]

50. Li, Y.; Dang, X.; Cao, D.; Chai, X. One-pot two steps synthesis of 4-nitropyrazole and its crystal structure. Chin. J. Energ. Mater. 2018, 22, 872–879.

51. Corte, J.R.; De Lucca, L.; Fang, T.; Yang, W.; Wang, Y.; Dilger, A.K.; Pabbisetty, K.B.; Ewing, W.R.; Zhu, Y.; Wexler, R.R. Macrocycles with aromatic P2 groups as factor xia inhibitors. U.S. Patent No. 9,777,001, 3 October 2017.

52. Ioannidis, S.; Talbot, A.C.; Follows, B.; Buckmelter, A.J.; Wang, M.; Campbell, A.M.; Schmidt, D.R.; Guerin, D.J.; Caravella, J.A.; Diebold, R.B. Preparation of Pyrrole and Pyrazolopyrimidines as Ubiquitin-Specific Protease Inhibitors. US patent 2,016,018,578,5A, 30 June 2016.

53. Han, S.J.; Kim, H.T.; Joo, J.M. Direct C–H Alkenylation of Functionalized Pyrazoles. J. Org. Chem. 2016, 81, 689–698. [CrossRef]

54. Deng, M.; Wang, Y.; Zhang, W.; Zhang, Q. Synthesis and Properties of 5-Methyl-4-nitro-1H-pyrazol-3(2H)-one and its Energetic Ion Compounds. Chin. J. Energ. Mater. 2017, 25, 646–650.

55. Pan, Y.; Wang, Y.; Zhao, B.; Gao, F.; Chen, B.; Liu, Y. Research Progress in Synthesis, Properties and Applications of Nitropyrazoles and Their Derivatives. Chin. J. Energ. Mater. 2018, 26, 796–812.

56. Yin, P.; Zhang, J.; He, C.; Parrish, D.A.; Shreeve, J.N.M. Polynitro-substituted pyrazoles and triazoles as potential energetic materials and oxidizers. J. Mater. Chem. A 2014, 2, 3200–3208. [CrossRef]
81. Li, Y.; Guo, J.; Song, L. Synthesis, performance and crystal structure of 1-methyl-3, 4-dinitropyrazole. *Chin. J. Explo. Propell.* 2015, 38, 64–68.
82. Zhang, Q.; Li, Y.; Qiao, Q.; Ren, H.; Li, Y. Optimization on synthesis process and characterization of 1-methyl-3,4-dinitropyrazoles. *Chin. J. Energ. Mater.* 2015, 23, 222–225.
83. Wang, Y.-L.; Zhang, Z.-Z.; Wang, B.-Z.; Zheng, X.-D.; Zhou, Y.-S. Synthesis of 3, 5-Dinitropyrazole. *Chin. J. Energ. Mater.* 2007, 15, 574–576.
84. Zaitsev, A.A.; Dalinger, I.L.; Shevelev, S.A. Dinitropyrazoles. *Russ. Chem. Rev.* 2009, 78, 589. [CrossRef]
85. Zhao, X.; Qi, C.; Zhang, L.; Wang, Y.; Li, S.; Zhao, F.; Pang, S. Amination of nitroazoles—A comparative study of structural and energetic properties. *Molecules* 2014, 19, 896–910. [CrossRef] [PubMed]
86. Wang, Y.-L.; Zhang, Z.-Z.; Wang, B.-Z.; Luo, Y.-F. Synthesis of LLM-116 by VNS Reaction. *Chin. J. Explo. Propell.* 2007, 30, 20–23.
87. Stefan, E.; Latyppov, N.V. Four Syntheses of 4-Amino-3, 5-dinitropyrazole. *J. Heterocyclic. Chem.* 2014, 51, 1621–1627.
88. Zhang, M.; Gao, H.; Li, C.; Fu, W.; Tang, L.; Zhou, Z. Towards improved explosives with a high performance: N-(3, 5-dinitro-1H-pyrazol-4-yl)-1 H-tetrazol-5-amine and its salts. *J. Mater. Chem. A* 2017, 5, 1769–1777. [CrossRef]
89. Dalinger, I.L.; Vatsadze, I.A.; Shkineva, T.K.; Popova, G.P.; Shevelev, S.A. Efficient procedure for high-yield synthesis of 4-substituted 3, 5-dinitropyrazoles using 4-chloro-3, 5-dinitropyrazole. *Synthesis* 2012, 44, 2058–2064. [CrossRef]
90. He, C.; Zhang, J.; Parrish, D.A.; Jean’ne, M.S. 4-Chloro-3, 5-dinitropyrazole: A precursor for promising insensitive energetic compounds. *J. Mater. Chem. A* 2013, 1, 2863–2868. [CrossRef]
91. Zhang, Y.; Huang, Y.; Parrish, D.A.; Jean’ne, M.S. 4-Amino-3, 5-dinitropyrazolate salts—highly insensitive energetic materials. *J. Mater. Chem.* 2011, 21, 6891–6897. [CrossRef]
92. Chavez, D.E.; Bottaro, J.C.; Petrie, M.; Parrish, D.A. Synthesis and Thermal Behavior of a Fused, Tricyclic 1, 2, 3, 4-Tetrazine Ring System. *Angew. Chem. Int. Ed.* 2015, 54, 12973–12975. [CrossRef]
93. Hervé, G.; Roussel, C.; Graindorge, H. Selective Preparation of 3, 4, 5-Trinitro-1H-Pyrazole: A Stable All-Carbon-Nitrated Aren. *Angew. Chem. Int. Ed.* 2010, 49, 3177–3181. [CrossRef]
94. Bölter, M.F.; Klapötke, T.M.; Kustermann, T.; Lenz, T.; Stierstorfer, J. Improving the Energetic Properties of Dinitropyrazoles by Utilization of Current Concepts. *Eur. J. Inorg. Chem.* 2018, 2018, 4125–4132. [CrossRef]
95. Yin, P.; Mitchell, L.A.; Parrish, D.A.; Shreeve, J.M. Comparative Study of Various Pyrazole-based Anions: A Promising Family of Ionic Derivatives as Inensitive Energetic Materials. *Chem.-Asian J.* 2017, 12, 378–384. [CrossRef] [PubMed]
96. Zhang, Y.; Parrish, D.A.; Shreeve, J.N.M. 4-Nitramino-3, 5-dinitropyrazole-Based Energetic Salts. *Chem.-Eur. J.* 2012, 18, 987–994. [CrossRef] [PubMed]
97. Kumari, D.; Balakhshe, R.; Banerjee, S.; Singh, H. Energetic plasticizers for gun & rocket propellants. *Rev. J. Chem.* 2012, 2, 240–262.
98. Dalinger, I.L.; Shakhnes, A.K.; Monogarov, K.A.; Suponitsky, K.Y.; Sheremetev, A.B. Novel highly energetic pyrazoles: N-fluorodinitromethyl and N-[(difluoroamino)dinitromethyl] derivatives. *Mendeleev Commun.* 2015, 25, 429–431. [CrossRef]
99. Dalinger, I.L.; Suponitsky, K.Y.; Pivkina, A.N.; Sheremetev, A.B. Novel Melt-Castable Energetic Pyrazole: A Pyrazolyl-Furazan Framework Bearing Five Nitro Groups. *Propel. Explos. Pyrot.* 2016, 41, 789–792. [CrossRef]
100. Agrawal, J.P.; Past, P. Future of Thermally Stable Explosives. *Cent. Eur. J. Energ. Mater.* 2012, 9, 273–290.
101. Li, C.; Zhang, M.; Chen, Q.; Li, Y.; Gao, H.; Fu, W.; Zhou, Z. 1-(3,5-Dinitro-1H-pyrazol-4-yl)-3-nitro-1H-1,2,4-triazol-5-amine (HCPT) and its energetic salts: Highly thermally stable energetic materials with high-performance. *Dalton Trans.* 2016, 45, 17956–17965. [CrossRef]
102. Wu, J.; Cao, D.; Wang, J.; Liu, Y.; Li, Y. Progress on 3,4,5-Trinitro-1H-pyrazole and Its derivatives. *Chin. J. Energ. Mater.* 2016, 24, 1121–1130.
103. Ravi, P.; Tewari, S.P. Facile and environmentally friendly synthesis of nitropyrazoles using montmorillonite K-10 impregnated with bismuth nitrate. *Catal. Commun.* 2012, 19, 37–41. [CrossRef]
104. Ravi, P.; Gore, G.M.; Sikder, A.K.; Tewari, S.P. Thermal decomposition kinetics of 1-methyl-3, 4, 5-trinitropyrazole. *Thermochim. acta* 2012, 528, 53–57. [CrossRef]
105. Dalinger, I.L.; Vatsadze, I.A.; Shkineva, T.K.; Popova, G.P.; Shevelev, S.A. The specific reactivity of 3, 4, 5-trinitro-1H-pyrazole. *Mendeleev Commun*. 2010, 20, 253–254. [CrossRef]

106. Dalinger, I.L.; Vatsadze, I.A.; Shkineva, T.K.; Popova, G.P.; Shevelev, S.A.; Nelyubina, Y.V. Synthesis and Comparison of the Reactivity of 3, 4, 5-1H-Trinitropyrazole and Its N-Methyl Derivative. *J. Heterocyclic Chem.* 2013, 50, 911–924. [CrossRef]

107. Guo, H.-J.; Dang, X.; Yang, F; Cao, D.-L.; Li, Y.-X.; Hu, W.-H.; Jiang, Z.-M.; Li, Z.-H.; Li, Z.-Y.; Zhang, L.-W. Solubility and thermodynamic properties of a kind of explosives in four binary solvents. *J. Mol. Liq.* 2017, 247, 313–327. [CrossRef]

108. Jun, W.; Mei, J.; Zhang, X.-Y. Empirical calculation of the explosive parameters of nitrodiazole explosives (II). *Chin. J. Energ. Mater.* 2013, 21, 609–611.

109. Zhang, Y.; Guo, Y.; Joo, Y.H.; Parrish, D.A.; Shreeve, J.N.M. 3, 4, 5-Trinitropyrazole-Based Energetic Salts. *Chem.-Eur. J.* 2016, 14, 9220–9228. [CrossRef]

110. Drukenmüller, I.E.; Klapötke, T.M.; Morgenstern, Y.; Rusan, M.; Stierstorfer, J. Metal Salts of Dinitro-, Trinitropyrazole, and Trinitroimidazole. *Z. Anorg. Allg. Chem.* 2014, 640, 2139–2148. [CrossRef]

111. Zhang, Y.; Parrish, D.A.; Jean’ne, M.S. Synthesis and properties of 3, 4, 5-trinitropyrazole-1-ol and its energetic salts. *J. Mater. Chem.* 2012, 22, 12659–12665. [CrossRef]

112. Kumar, D.; He, C.; Mitchell, L.A.; Parrish, D.A.; Shreeve, J.N.M. Connecting energetic nitropyrazole and aminotetrazole moieties with N,N′-ethylene bridges: A promising approach for fine tuning energetic properties. *J. Mater. Chem.* 2016, 4, 9220–9228. [CrossRef]

113. Kumar, D.; Imler, G.H.; Parrish, D.A.; Shreeve, J.N.M. N-Acetonitrile Functionalized Nitropyrazoles: Precursors to Insensitive Asymmetric N-Methylene-C Linked Azoles. *Chem.-Eur. J.* 2017, 23, 7876–7881. [CrossRef]

114. Tang, Y.; Kumar, D.; Shreeve, J.N.M. Balancing excellent performance and high thermal stability in a dinitropyrazole fused 1, 2, 3, 4-tetrazine. *J. Am. Chem. Soc.* 2017, 139, 13684–13687. [CrossRef] [PubMed]

115. Tang, Y.; He, C.; Imler, G.H.; Parrish, D.A.; Jean’ne, M.S. AC–C bonded 5, 6-fused bicyclic energetic molecule: Exploring an advanced energetic compound with improved performance. *Chem. Commun.* 2018, 54, 10566–10569. [CrossRef] [PubMed]

116. Tang, Y.; He, C.; Imler, G.H.; Parrish, D.A.; Jean’ne, M.S. Energetic derivatives of 4, 4′, 5′-tetrinitro-2 H, 2′H-3, 3′-bipyrazole (TNBP): Synthesis, characterization and promising properties. *J. Mater. Chem. A* 2018, 6, 5136–5142. [CrossRef]

117. Domasevitch, K.V.; Gospodinov, I.; Krautschek, H.; Klapötke, T.M.; Stierstorfer, J. Facile and selective polynitrations at the 4-pyrazolyl dual backbone: Straightforward access to a series of high-density energetic materials. *New J. Chem.* 2019, 43, 1305–1312. [CrossRef]

118. Kumar, D.; Mitchell, L.A.; Parrish, D.A.; Shreeve, J.N.M. Asymmetric N,N′-ethylene-bridged azole-based compounds: Two way control of the energetic properties of compounds. *J. Mater. Chem. A* 2016, 4, 9931–9940. [CrossRef]

119. Yin, P.; Parrish, D.A.; Shreeve, J.M. Bis(nitroamino-1,2,4-triazolates): N-bridging strategy toward insensitive energetic materials. *Angew. Chem. Int. Ed.* 2014, 53, 12889–12892. [CrossRef]

120. Zhang, Q.; Zhang, J.; Parrish, D.A.; Shreeve, J.N.M. Energetic N-Trinitroethyl-Substituted Mono-, Di-, and Triaminotetrazolates. *Chem.-Eur. J.* 2013, 19, 11000–11006. [CrossRef]

121. Joo, Y.H.; Shreeve, J.N.M. Energetic Mono-, Di-, and Trisubstituted Nitroiminotetrazolates. *Angew. Chem. Int. Ed.* 2009, 48, 564–567. [CrossRef]

122. Yin, P.; Zhang, J.; Parrish, D.A.; Shreeve, J.M. Energetic N,N′-ethylene-bridged bis(nitropyrazoles): Diversified functionalities and properties. *Chemistry 2014*, 20, 16529–16536. [CrossRef]

123. Fischer, D.; Gottfried, J.L.; Klapotke, T.M.; Karaghissoff, K.; Stierstorfer, J.; Witkowski, T.G. Synthesis and Investigation of Advanced Energetic Materials Based on Bisparyloylethanones. *Angew. Chem. Int. Ed.* 2016, 55, 16132–16135. [CrossRef]

124. Li, H.; Zhang, L.; Petrutik, N.; Wang, K.; Ma, Q.; Shem-Tov, D.; Zhao, F.; Gozin, M. Molecular and crystal features of thermostable energetic materials: Guidelines for architecture of “bridged” compounds. *ACS Central Sci.* 2019, 6, 54–75. [CrossRef] [PubMed]

125. Zhang, M.X.; Pagoria, P.F.; Imler, G.H.; Parrish, D. Trimerization of 4-Amino-3,5-dinitropyrazole: Formation, Preparation, and Characterization of 4-Diazo-3,5-bis(4-amino-3,5-dinitropyrazol-1-yl) pyrazole (LLM-226). *J. Heterocyclic Chem.* 2019, 56, 781–787. [CrossRef]
126. Yan, T.; Cheng, G.; Yang, H. 1,2,4-Oxadiazole-Bridged Polynitropyrazole Energetic Materials with Enhanced Thermal Stability and Low Sensitivity. *ChemPlusChem* 2019, 84, 1567–1577. [CrossRef] [PubMed]

127. Yan, T.; Cheng, G.; Yang, H. 1,3,4-Oxadiazole based thermostable energetic materials: Synthesis and structure–property relationship. *New J. Chem.* 2020, 44, 6643–6651. [CrossRef]

128. Yin, P.; Zhang, J.; Imler, G.H.; Parrish, D.A.; Shreeve, J.N.M. Polynitro-Functionalized Dipropyrazol-1, 3, 5-triazinanes: Energetic Polycyclization toward High Density and Excellent Molecular Stability. *Angew. Chem. Int. Ed.* 2017, 129, 8960–8964. [CrossRef]

129. Il'yasov, S.G.; Danilova, E.O. Preparation of 1,3-Diazido-2-Nitro-2-Azapropane from Urea. *Propell. Explos. Pyrot.* 2012, 37, 427–431. [CrossRef]

130. Zhang, J.; He, C.; Parrish, D.A.; Shreeve, J.M. Nitramines with Varying Sensitivities: Functionalized Dipyrazolyl-N-nitromethanamines as Energetic Materials. *Chem.-Eur. J.* 2013, 19, 8929–8936. [CrossRef]

131. Klapötke, T.M.; Penger, A.; Pflüger, C.; Stierstorfer, J.; Suceska, M. Advanced Open-Chain Nitramines as Energetic Materials: Heterocyclic-Substituted 1,3-Dichloro-2-nitrazapropane. *Eur. J. Inorg. Chem.* 2013, 2013, 4667–4678. [CrossRef]

132. Yin, P.; Zhang, J.; Mitchell, L.A.; Parrish, D.A.; Shreeve, J.N.M. 3,6-Dinitropyrazolo[4,3-c]pyrazole-Based Multipurpose Energetic Materials through Versatile N-Functionalization Strategies. *Angew. Chem. Int. Ed.* 2016, 128, 13087–13089. [CrossRef]

133. Pagoria, P.F. Synthesis, Scale-up and Experimental Testing of ANPZO. In Proceedings of the 1998Insensitive Munitions and Energetic Materials Technology Symposium, San Diego, CA, USA, 16–19 November 1998.

134. Dalinger, I.L.; Shkineva, T.K.; Shevelev, S.A.; Kanishchev, M.I.; Kral, V.; Arnold, Z. A method for preparation of C-diformylmethylnitropyrazoles. *Russ. Chem. Bull.* 1993, 42, 211–212. [CrossRef]

135. Yin, P.; Zhang, J.; Mitchell, L.A.; Parrish, D.A.; Shreeve, J.N.M. 3,6-Dinitropyrazolo[4,3-c]pyrazole-Based Multipurpose Energetic Materials through Versatile N-Functionalization Strategies. *Angew. Chem. Int. Ed.* 2016, 128, 13087–13089. [CrossRef]

136. Li, Y.; Wang, B.; Luo, Y.; Yang, W.; Wang, Y.; Li, H. Synthesis of 3,6-Dinitropyrazolo[4,3-c]pyrazole (DNPP) in Hectogram scale and Crystal Structure of DNPP·H$_2$O. *Chin. J. Energ. Mater.* 2013, 21, 449–454.

137. Luo, Y.; Ge, Z.; Wang, B.; Zhang, H.; Liu, Q. Synthetic improvment of DNPP. *Chin. J. Energ. Mater.* 2007, 15, 205–208.

138. Zhang, J.; Parrish, D.A.; Shreeve, J.M. Thermally sTable 3,6-dinitropyrazolo[4,3-c]pyrazole-based energetic materials. *Chem.-Asian J.* 2014, 9, 2953–2960. [CrossRef]

139. Li, Y.; Li, X.; Li, H.; Lian, P.; Yifen, L.; Wang, B. Synthesis and thermal performance of organic diamino salts of 3,6-dinitropyrazol04,3-cpyrazole (DNPP). *J. Solid Rocket Technol.* 2015, 38.

140. Li, Y.; Chang, P.; Chen, T.; Hu, J.; Wang, B.; Zhang, H.; Li, P.; Wang, B. Synthesis, Thermal Performance and Quantum Chemistry Study on 1,4-Diamino-3,6-dinitropyrazolo[4,3-c]pyrazole. *Chin. J. Energ. Mater.* 2012, 32, 580. [CrossRef]

141. Li, Y.; Chang, P.; Chen, T.; Hu, J.; Wang, B.; Zhang, H.; Li, P.; Wang, B. Synthesis, Crstal Structure and Properties of 1,4-Dinitramino-3,6-dinitropyrazolo[4,3-c]pyrazole’s Aminourea Salt. *Chin. J. Explos. Propell.* 2019, 42, 341–345.
145. Zhang, W.; Xia, H.; Yu, R.; Zhang, J.; Wang, K.; Zhang, Q. Synthesis and Properties of 3, 6-Dinitropyrazolo [4, 3-c]-pyrazole (DNPP) Derivatives. *Propell. Explos. Pyrot.* **2020**, *45*, 546–553. [CrossRef]

146. Xia, H.; Zhang, W.; Jin, Y.; Song, S.; Wang, K.; Zhang, Q. Synthesis of Thermally Stable andInsensitive Energetic Materials by Incorporating the Tetrazole Functionality into a Fused-Ring 3,6-Dinitropyrazolo-[4,3-c]Pyrazole Framework. *ACS Appl. Mater. Inter.* **2019**, *11*, 45914–45921. [CrossRef] [PubMed]

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).