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Nitro-tetrazole based high performing explosives: Recent overview of synthesis and energetic properties

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ABSTRACT

Heterocyclic skeleton (Azoles) and different energetic groups containing high performing explosives are highly emerged in recent years to meet the challenging requirements of energetic materials in both military and civilian applications with improved performance. For this purpose tetrazole (Azole) is identified as an attractive heterocyclic backbone with energetic functional groups nitro (-NO_2), nitrato (-ONO_2), nitrimino (-NNO_2), and nitramino (−NH−NO_2) to replace the traditionally used high performing explosives. The tetrazole based compounds having these energetic functional groups demonstrated advanced energetic performance (detonation velocity and pressure), densities, and heat of formation (HOF) and became a potential replacement of traditional energetic compounds such as RDX. This review presents a summary of the recently reported nitro-tetrazole energetic compounds containing poly-nitro, di/mono-nitro, nitrato/nitramino/nitrimino, bridged/bis/di tetrazole and nitro functional groups, describing their preparation methods, advance energetic properties, and further applications as high-performing explosives, especially those reported in the last decade. This review aims to provide a fresh concept for designing nitro-tetrazole based high performing explosives together with major challenges and perspectives.

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1. Introduction

In modern times, life without high performing explosives is considered impossible due to their extensive use during peace time and armed conflicts. Therefore, to fulfill the demand, many researchers all over the world are working to develop modern energetic materials based high performing explosives with enhanced insensitivity [1,2]. The design and synthesis of new high performing explosive as energetic materials remain an interesting area of research in material sciences to replace the traditional high performing explosives [3–5]. The fundamental properties of high performing explosives include the ratio of C/H/N, density, the heat of formation (HOF), sensitivity towards impact as well as friction, thermal stability, detonation performance (velocity and pressure), and acceptability to the environment [6,7]. The traditional energetic compounds containing oxygen, hydrogen, and nitrogen includes 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazine (RDX) and 1,3,5,7-tetranitro-1,3,5,7tetrazoctane (HMX), Pentaerythritol tetranitrate (PETN), 2,4,6-triamino-1,3,5-trinitrobenzene (TATB), octanitrocubane (ONC) and Hexanitrohexaazaisowurtzitane (CL-20) (Fig. 1) [8–13]. Unfortunately, the release of most of these nitro functional groups containing high-performance explosives often contaminated the surface, groundwater, soils, and sediments, which makes them highly non-desirable [14,15]. Therefore, the synthesis of high nitrogen-containing energetic materials is promoted to fulfill the requirements of future defense and space sectors. The energy of these nitrogen-rich compounds comes from high HOF unlike the intramolecular oxidation of a carbon backbone in traditional high-performance explosives [16].

In recent years heterocyclic skeleton (Azoles) based compounds with improved performance, have emerged to meet the challenging requirements of energetic materials [17–20]. In addition, combining various energetic groups with different heterocyclic backbones is one of the most significant and modern techniques to develop novel high-performing explosives [21–24]. In this regard, tetrazole is found to be an attractive heterocyclic backbone for the synthesis of modern high performing explosives due to the practical significance and variety of properties [25–27]. The structure of

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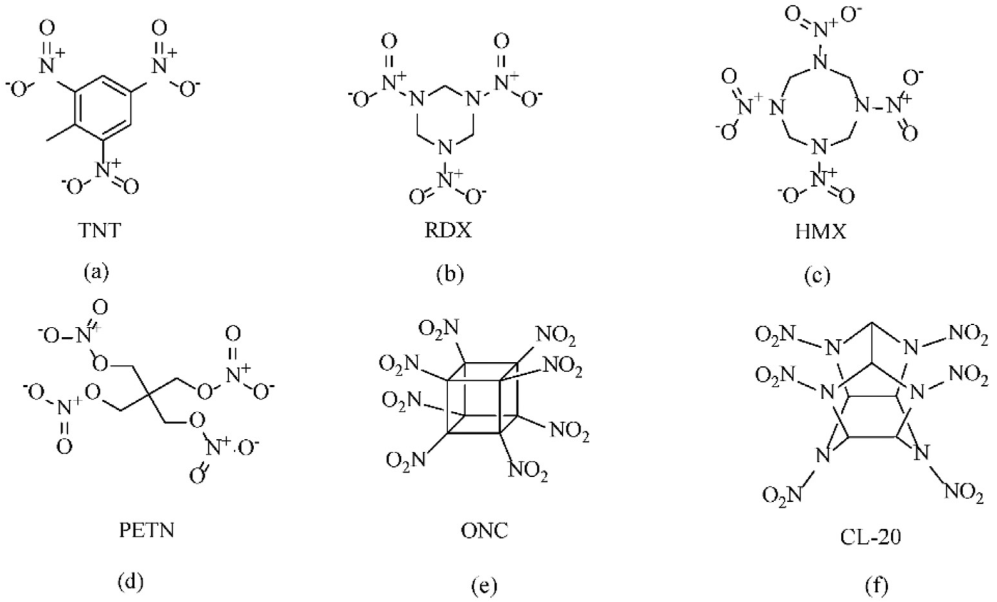

TNT (a) RDX (b) HMX (c) PETN (d) ONC (e) CL-20 (f)

Fig. 1. Traditional high-performing energetic materials based on different backbones.

tetrazole contains 79.8% nitrogen content and a large number of N—N and C—N due to that it conserves more energy than the other azole derivatives. The tetrazole possessed a high HOF of 320 kJ/mol due to the presence of a large number of nitrogen-nitrogen bonds, high density, and ring strain which are important properties required for the development of high-performing explosives [28,29]. Furthermore, the physical and energetic properties of tetrazole based compounds can be easily improved by the introduction or replacement of energetic functional groups as substituents on the ring. The interesting energetic properties and unique chemical structure combinations have an attraction for researchers to this novel class of compounds. The combination of tetrazole moiety and energetic functional groups produces many new energetic materials to meet the challenging requirements of high performing explosive. Therefore, for this purpose, the tetrazole combined framework with the nitro (-NO_2), nitrato (-ONO_2), nitrimino (-NNO_2), and nitramino (—NH—NO_2) energetic functional groups could result in favorable energetic performance [30,31]. However, the achievement of species containing these energetic functional groups is still challenging owing to the high sensitivity and low thermal stability. The properties of most of them either predicted theoretically or exist only under specific conditions.

In this review, the current developments in the field of tetrazole based energetic compounds containing energetic functional groups (-NO_2, —ONO_2, —NNO_2, and —NH—NO_2) were designed and synthesized are discussed since 2010. Most of the energetic compounds highlighted here exhibit appropriate properties to be classified as high performing explosives. The properties of these compounds such as density, thermal decomposition temperature, HOF, detonation performance (detonation pressure and velocity), impact sensitivity, and friction sensitivity are reviewed in detail. TNT, TATB, RDX, HMX, and CL-20 are used as conventional high-performance explosives for comparison as listed in Table 1 [32]. It is expected that this review will present a summary of the major methodologies used for the design and synthesis of tetrazole holding energetic compounds with —NO_2, —ONO_2, —NNO_2, and —NH—NO_2 energetic functional groups. While the comparison of these synthesized compounds with standard conventional high-performance explosives will stimulate more research to proposed similar energetic compounds with advanced properties.

Table 1
Physicochemical and energetic properties of typically used energetic compounds [18,33].

Compound	T_d [a] /°C	d [b]/ $(g\cdot cm^{-3})$	D [c] $/(m\cdot s^{-1})$	P [d] /GPa	IS [e] /J	FS [f] /N	$\triangle H_f$ [g] $/(kJ\cdot mol^{-1})$
TNT	295	1.65	7303	21.3	15	353	−59.3
TATB	360	1.94	8544	32.1	50	360	−154.2
RDX	210	1.80	8795	34.9	7.5	120	70.7
HMX	280	1.91	9144	39.2	7	120	74.8
CL-20	210	2.04	9706	45.2	4	94	397.8

Note: In this review, all the quantity symbols are used in Tables.
[a] Decomposition temperature (onset).
[b] Density.
[c] Detonation velocity (calculated).
[d] Detonation pressure (calculated).
[e] Impact sensitivity.
[f] Friction sensitivity.
[g] The heat of formation (calculated).

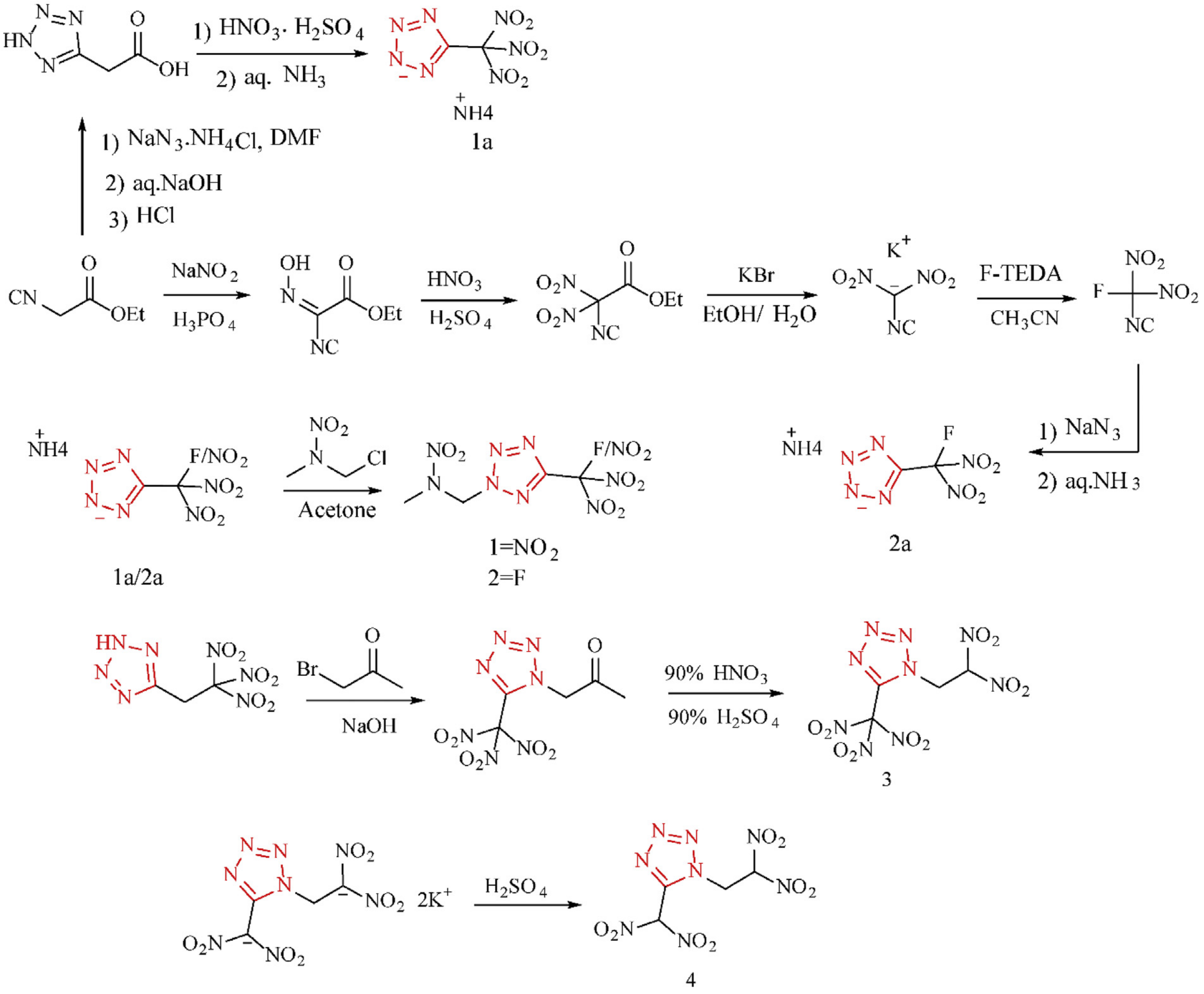
2. Energetic compounds based on tetrazole framework in a combination of nitro groups (-NO_2, —ONO_2, —NNO_2, and —$NHNO_2$)

In the development of high energy explosives, the main focus is on the basic skeleton of compound (such as pentazole, tetrazole, triazole, pyrazole, etc.), and energetic substituents [34,35]. Tetrazole is considered as one of the ideal organic frameworks for the synthesis of high energy explosive owing to the high nitrogen content and stability [36]. In addition, the compounds containing energetic groups such as nitro (-NO_2), nitrato (-ONO_2), nitrimino (-NNO_2), and nitriamino (—NH—NO_2) are of special interest [37]. These groups are important to attain desirable energetic properties owing to their high density, HOF, and good oxygen balance [38—41]. Currently, the combination of a tetrazole along with these energetic moieties (-NO_2, —ONO_2, —NNO_2, and —NH—NO_2) has widely used to get satisfactory properties for high energy explosives [42,43]. However, the insensitivity and high energy are found contradictory which makes the development of these new high energy explosives an interesting and challenging work [44,45].

2.1. Poly-nitro groups containing tetrazole based compounds

The incorporation of the poly-nitro groups to the heterocyclic compounds is interesting to prepare high-performing explosives with advance energetic properties [46,47]. In continuing effort the polynitro group containing tetrazole based compounds 1 and 2 were synthesized according to the procedure given in Scheme 1 [48]. The synthesis was originated from commercially accessible ethyl 2-cyanoacetate. The synthesis of 1a (ammonium 5-(fluorodinitromethyl)-2 H-tetrazolate) was conducted by using decarboxylative nitration of ethyl 2-(1H-tetrazol-5-yl)acetate [49]. Further, ammonium 5-(fluorodinitromethyl)-2 H-tetrazolate (2a) was attained from potassium dinitroacetonitrile, and the addition of NaN_3, modified from the reported method to maintain stability. Differing from the literature the fluorination of potassium dinitroacetonitrile was performed with Selectfluor in anhydrous acetonitrile at ambient temperature in a closed vessel to attain the compound 1a. The alkylation reactions of compounds 1a and 2a were performed with 2-nitro-2-azapropyl chloride in anhydrous acetone, furnishing the 2-(2-nitro-2-azapropyl)-5-(polynitromethyl)-2H-tetrazoles 1 and 2 as colorless crystalline solids in good yields of 78% each. The physiochemical and energetic properties of these prepared compounds 1 and 2 are listed in Table 2. The obtained densities were 1.75–1.83 g/cm^3 and detonation velocities were 8704 and 8773 m/s which were higher than to TNT and comparable RDX in the case of compound **2**. While the detonation pressure of compounds 1 and 2 was 33.4 and 34.2 GPa respectively, which are comparable to RDX. These compounds were obsessed with high positive HOFs. Whereas, these compounds were found thermally less stable (134 and 184 °C) owing to their high sensitivity towards impact and friction. Hence, due to high density and detonation performance (velocity and pressure), compound 1, and 2 can be used as high performance explosive.

The synthesis of compound 3 was attained by using 5 (Trinitromethyl)-2H-tetrazole which has a density [49] of 1.92 g/cm^3 as described in Scheme 1 [50,51]. At first, the 5 (Trinitromethyl)-2H-tetrazole was allowed to react with Bromo acetone to produce an intermediate compound 1-(5-(trinitromethyl)-1H-tetrazol-1-yl) propan-2-one, which further undergoes nitration with a nitrating mixture (HNO_3 + H_2SO_4) to achieve the targeted compound 3. Furthermore, the potassium salt of 3 was synthesized to achieve another compound 2,5-bis(dinitromethyl)-2H-tetrazole (4) after the acidification with sulfuric acid. The prepared compounds 3 and 4 were thermally less stable (73 °C and 88 °C respectively) due to the presence of poly nitro groups. The densities of compounds 3 and 4 were 1.88 and 1.92 g/cm^3. Moreover, the detonation velocity and pressure of compound 3 was 8511 m/s and 31.2 GPa, and compound 4 was 9123 m/s and 37.9 GPa, which are higher than



Scheme 1. Synthetic pathway of poly-nitro groups containing tetrazole based compounds (1–4).

Table 2
Physiochemical and energetic properties of poly-nitro groups containing tetrazole based energetic compounds 1–23.

Compound	T_d /°C	d /(g·cm^{-3})	D /(m·s^{-1})	P /GPa	IS /J	FS /N	H_f /(kJ·mol^{-1})
1	134	1.75	8704	33.4	3	40	313.9
2	184	1.83	8773	34.2	2	36	98.3
3	73	1.88	8511	31.2	2	80	296.67
4	88	1.92	9123	37.7	3	120	259.98
5	150	1.85	8771	35.7	35.7	15	202.8
6	144	1.67	8115	27.6	27.6	19	168.2
7	148	1.71	8358	30.4	30.4	5	186.8
8	146	1.60	7859	24.9	24.9	36	96.2
9	183	1.79	8460	32.1	32.1	23	420.0
10	143	1.73	8256	29.3	29.3	36	414.5
11	166	1.66	7996	26.3	26.3	>40	382.1
12	146	1.84	8734	35.7	35.7	11	498.1
13	141	1.69	8122	27.5	27.5	>40	682.1
14	247	1.66	7954	24.6	>40	360	317.1
15	257	1.67	7889	23.2	>40	360	373.7
16	135	1.71	8172	27.1	30	240	430.7
17	246	1.61	7709	22.3	>40	360	278.1
18	265	1.65	7768	21.8	>40	360	364.6
19	134	1.67	7959	24.7	>40	360	437.3
20	182	1.77	9004	34.9	22	240	1091.8
21	223	1.69 (1.75)	7899	24.1	>40	–	369.0
22	93	1.76 (1.78)	8208	28.0	>40	–	495.4
23	175	1.83 (1.79)	8298	28.4	>40	–	470.5
TNT	295	1.65	7303	21.3	15	353	−59.3
TATB	360	1.94	8544	32.1	50	360	−154.2
RDX	210	1.80	8795	34.9	7.5	120	70.7
HMX	280	1.91	9144	39.2	7	120	74.8

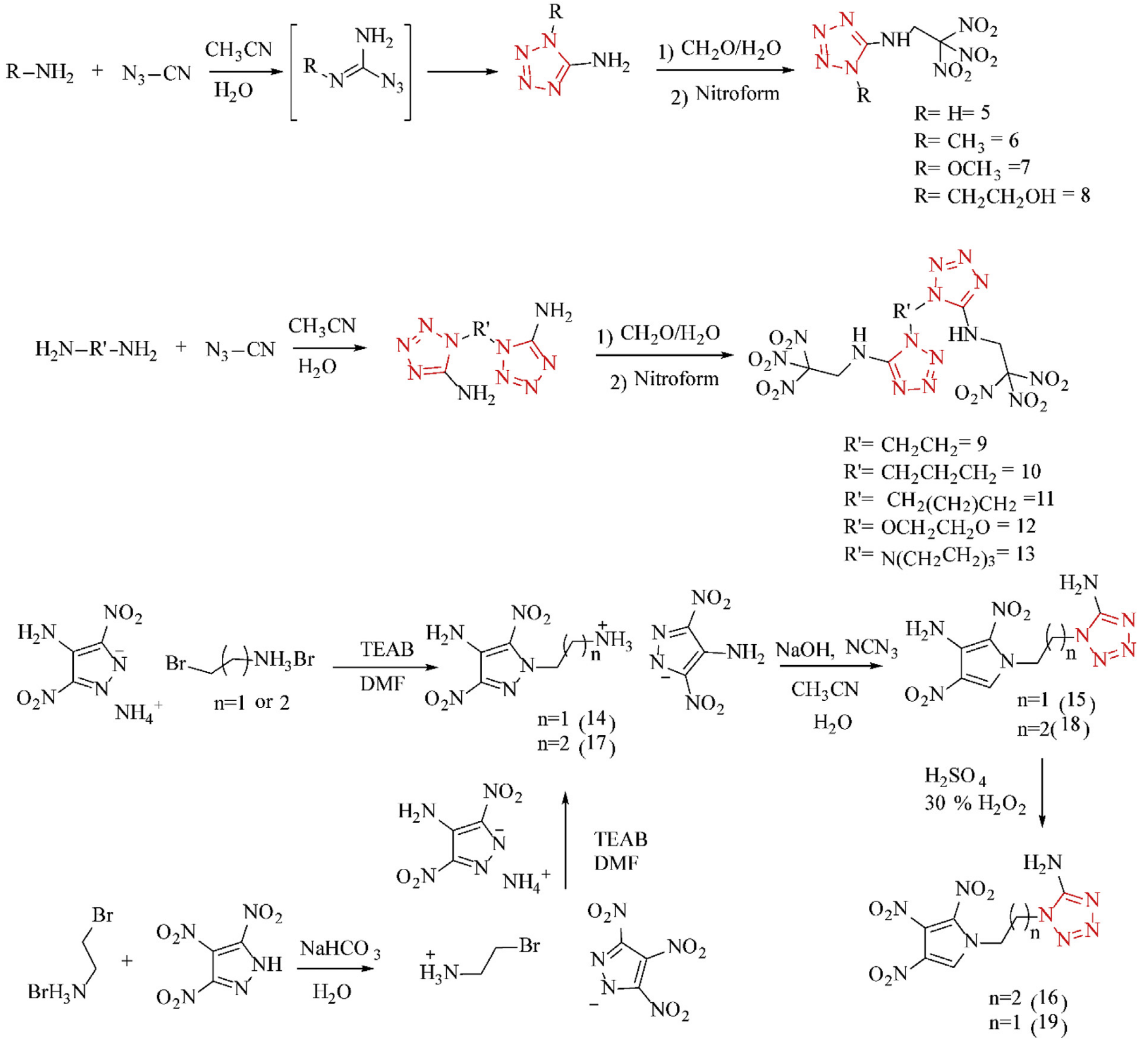
RDX and comparable to HMX. The calculated HOF for these compounds was high and oxygen balance was positive. Hence, poly nitro groups along with tetrazole play an important role to enhance the density and detonation performance of the targeted compounds.

A family of dense energetic compounds 5–13, N-trinitroethyl-substituted mono-, bis-, and tri-5-aminotetrazoles attained via reaction of a primary amine with cyanogen azide, tailed by the trinitroethyl functionalization (Scheme 2) [52]. The trinitroethyl functionality was introduced through condensation of a hydroxymethyl intermediate which was synthesized after the reaction of formaldehyde with trinitromethane. The synthesized energetic compounds 5–13 exhibited lower decomposition temperature as compared to standard high-performance explosives in the range of 141–183 °C as illustrated in Table 2. The measured densities were ranged from 1.60 to 1.85 g/cm^3, greater than RDX in the case of compounds 5 and 12 (1.84 and 1.84 g/cm^3). Whereas, most of the prepared compounds have lower densities due to the manifestation of the bulky space-oriented trinitroethyl group. The HOFs were positive and higher than standard energetic materials in the range of 96.2–682.2 kJ/mol. The calculated detonation velocity and pressure for these trinitroethyl-substituted compounds were fell in the range of 7859–8771 m/s and 24.9–35.7 GPa respectively, advance than TNT, and approaching RDX in the case of 5 and 12 (8771 & 8734 m/s and 35.7 & 35.7 GPa respectively). All the prepared compounds were sensitive towards impact (except 7 and 13) and friction. Although, these compounds particularly 5 and 12 retain good detonation performance, density, and HOF. However, their thermal stability and sensitivities towards impact and friction were not appropriate to use as high-performance explosives.

Poly nitro tetrazole energetic compounds 14–19 and their derivatives connected with pyrazole by *N*,*N*-ethylene/propylene bridges were synthesized as demonstrated in Scheme 2 [53]. The 4-amino-3,5-dinitropyrazolate was brought into contact with 2-bromoethylamine hydrobromide in the presence of phase transfer catalyst TEAB (tetraethylammonium bromide) to give 14, which was further used to achieve compound 15, an *N*,*N*-ethylene bridge compound bonded by 4-amino-3,5-dinitropyrazole with amino-tetrazole. The compound 16 was also synthesized by sodium trinitropyrazolate with 2-bromoethylamine hydrobromide and then reacted with ammonium 4-amino-3,5-dinitropyrazolate in the DMF and TEAB. The oxidation of 15 was ended with sulfuric acid and hydrogen peroxide to carry out the synthesis of 16. Whereas, the analogous propylene bridge compounds 17–19 were also prepared in the same way as 14–16 initiated through 3-bromopropylamine hydrobromide. The asymmetric *N*,*N*-ethylene/propylene bridges were decomposed in the range of 120 °C–267 °C as expressed in Table 2. The thermal stabilities of diamino compounds 15 and 18 were found higher (257 °C and 265 °C) than RDX and lower than TNT. The measured densities were greater than TNT expect compound 17 (1.61 g/cm^3) and less than other traditional high-performance explosives. In addition, due to the huge content of nitrogen, the HOF was found high positive as compared to RDX and TNT falling from 241.7 to 463.0 kJ/mol. The compounds 14, 15, and 17–19 were insensitive towards impact and friction. However, the detonation performance was the only advance than TNT in the range of 21.8–27.1 GPa (pressure) and 7709–8172 m/s. Therefore, owing to the presence of fewer nitro groups and a large number of carbon and hydrogen atoms the prepared energetic compounds were not better than standard high-performance explosives except TNT. Nevertheless, this technique can be used to attain better energetic compounds with enhanced sensitivities.

The starting reagent 4-amino-3-hydrazino-1,2,4-triazolelium chloride experiences cyclization with sodium azide and triethyl orthoformate to yield compound (1H-tetrazol-1-yl)-4H-1,2,4-triazole-3,4-diamine. The nitro groups containing compound 20 was synthesized by the reaction of (1H-tetrazol-1-yl)-4H-1,2,4-triazole-3,4-diamine with trinitroethanol as represented in Scheme 3 [54]. The thermal stability and density of compound 20 were 182 °C and 1.77 g/cm^3 respectively as listed in Table 1, which is not much reasonable as compared to standard high-performance explosives. The calculated density was only advanced than TNT and HOF was 1091.8 kJ/mol for multi-nitro groups containing compound 20. The detonation performance (velocity; 9004 and pressure; 34.9) was found comparable to RDX. Therefore, the high detonation performance and HOF of these compounds making them suitable to be used as high-performance explosives.

The perception of synthesis of small molecules that keep tetrazole with a high content of N and O- attained substantial attention due to their better performance and high thermal stability [55,56]. Therefore, the methoxy group of 1-(4-methoxy-3,5-dinitrophenyl)-1H-tetrazole was consumed to convert NH_2, NO_2, and $NH{-}NO_2$ to boost the energetic abilities as shown in Scheme 3 [57]. The methoxy group transformed directly to NH_2 and $NH{-}NO_2$ using aqueous ammonia and fuming nitric acid to conquer 21 and 22 respectively. Whereas, the oxidation 21 by sodium tungstate/H_2SO_4/H_2O_2 directed to the trinitro substituted aryl-tetrazole 23. The crystal density of compounds 22 and 23 (1.78 and 1.79 g/cm^3) was closer to RDX (Table 1). The detonation velocities for synthesized compounds 21–23 were 7899, 8208, and 8298 m/s respectively, which were closer to RDX. The decomposition temperature of compound 21 was 223 °C, which was comparable to RDX among others. The impact sensitivities of synthesized compounds 21 to 23 were >40 J. Thus, a large number of nitro groups enhanced the energetic abilities of the synthesized compounds. Furthermore, the synthesized compounds possess high positive HOFs due to the enrichment of nitrogen in the range of 293.7–882.5 kJ/mol essential factor for high-performance explosives. Hence, 23 was found captivating energetic material due to retaining better detonation performance, density, and insensitivity towards impact.

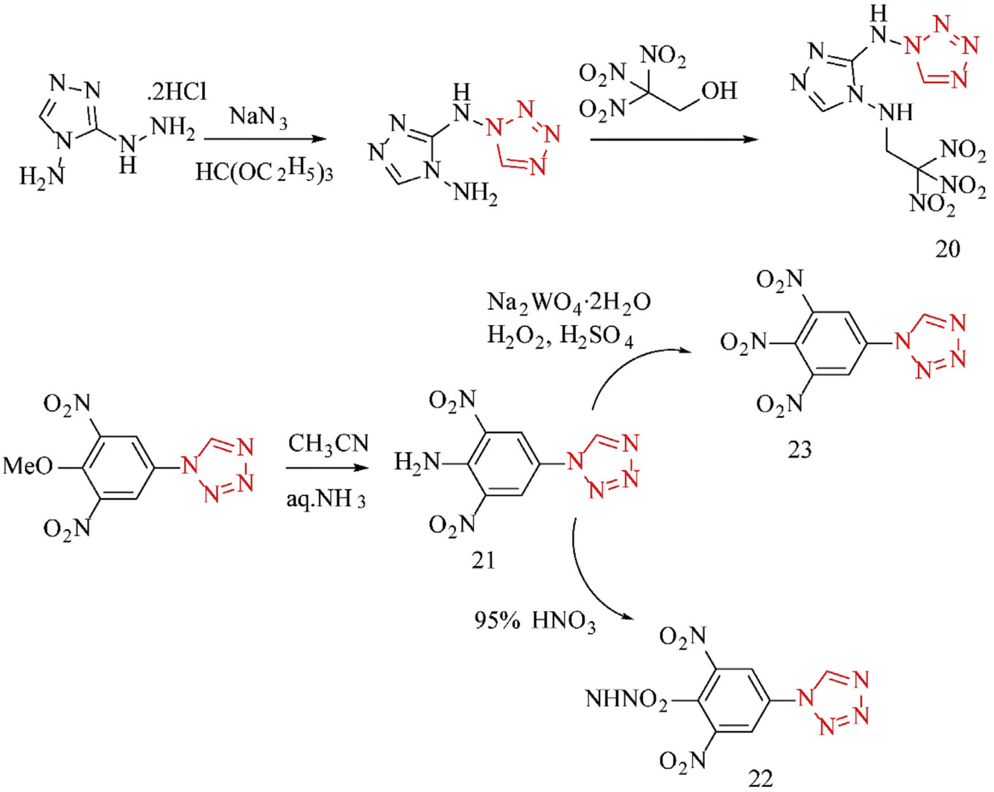


Scheme 2. Synthetic pathway of poly-nitro groups containing tetrazole based compounds (5-19).

2.2. Di/mono-nitro groups containing tetrazole based compounds

N-(3,5-dinitro-1H-pyrazol-4-yl)-1H-tetrazol-5-amine (24) energetic compound was achieved through the synthesis of 3,4,5-trinitro-1H-pyrazole (TNP) (Scheme 2) [12,58]. For the synthesis of TNP, the 4-chloro-1H-pyrazole as starting material was used, which subsequently undergoes nitration, amination, and oxidation [59]. The nitration was proceeding using concentrated HNO_3 and H_2SO_4 to afford 3,5-dinitro-4-chloropyrazole. The amination of 3,5-dinitro-4-chloropyrazole was achieved at 170 °C in a sealed tube with 25% aqueous ammonia. The obtained product was 3,5-dinitro-4-aminopyrazole (LLM-116) having an excellent yield of 85%. Following amination, the oxidation was accomplished in concentrated H_2SO_4 and 30% hydrogen peroxide to get TNP. Finally, the TNP was reacted with commercially available 5- amino-1H-tetrazole (ATZ) in 4 equivalent solution of KOH maintaining temperature in the range of 140–160 °C to produce the targeted compound. Furthermore, the product was acidified with 20% H_2SO_4 and recrystallized from ethanol-water to give the desired deep yellow solid compound with 63% yield. This compound was found thermally more stable than RDX as required for high-performance explosives (Table 3). The density and HOF were 1.86 g/cm^3 and 856.4 kJ/mol, which were greater than RDX. In addition, the detonation velocity and pressure of the compound were 9289 m/s and 38.6 GPa respectively. The detonation pressure was higher than RDX and lower than HMX. While the detonation velocity was higher than RDX and comparable to HMX. Thus, compound 24 with a distinctive assembly of polynitropyrazole and nitrogen-rich tetrazole moiety bridged by nitrogen atoms have high thermal stability, detonation performance, and acceptable impact and friction sensitivities can be used as high performance explosive.

The energetic compound 5-(5-amino-2H-1,2,3-triazol-4yl)-1H-tetrazole and its nitro derivative 24 was prepared as shown in Scheme 4 [60]. The main compound 5-(5-amino-2H-1,2,3-triazol-4yl)-1H-tetrazole was prepared in five steps using benzyl azide and cyanoacetamide with sodium in ethanol to get 5-amino-1benzyl-1,2,3-triazole-4-carboxamide. In the next step benzyl protective group was remain on the triazole and treated with trifluoroacetic acid, which was further reacted with sodium azide to carried out the synthesis of 5-(5-amino-1-benzyl-1,2,3-triazol-4-yl)tetrazole. In the final step, the debenzylation of 1-benzyl-4-(1H-tetrazol-5-yl)-1H-1,2,3-triazol-5-amine was conducted with sodium in liquid



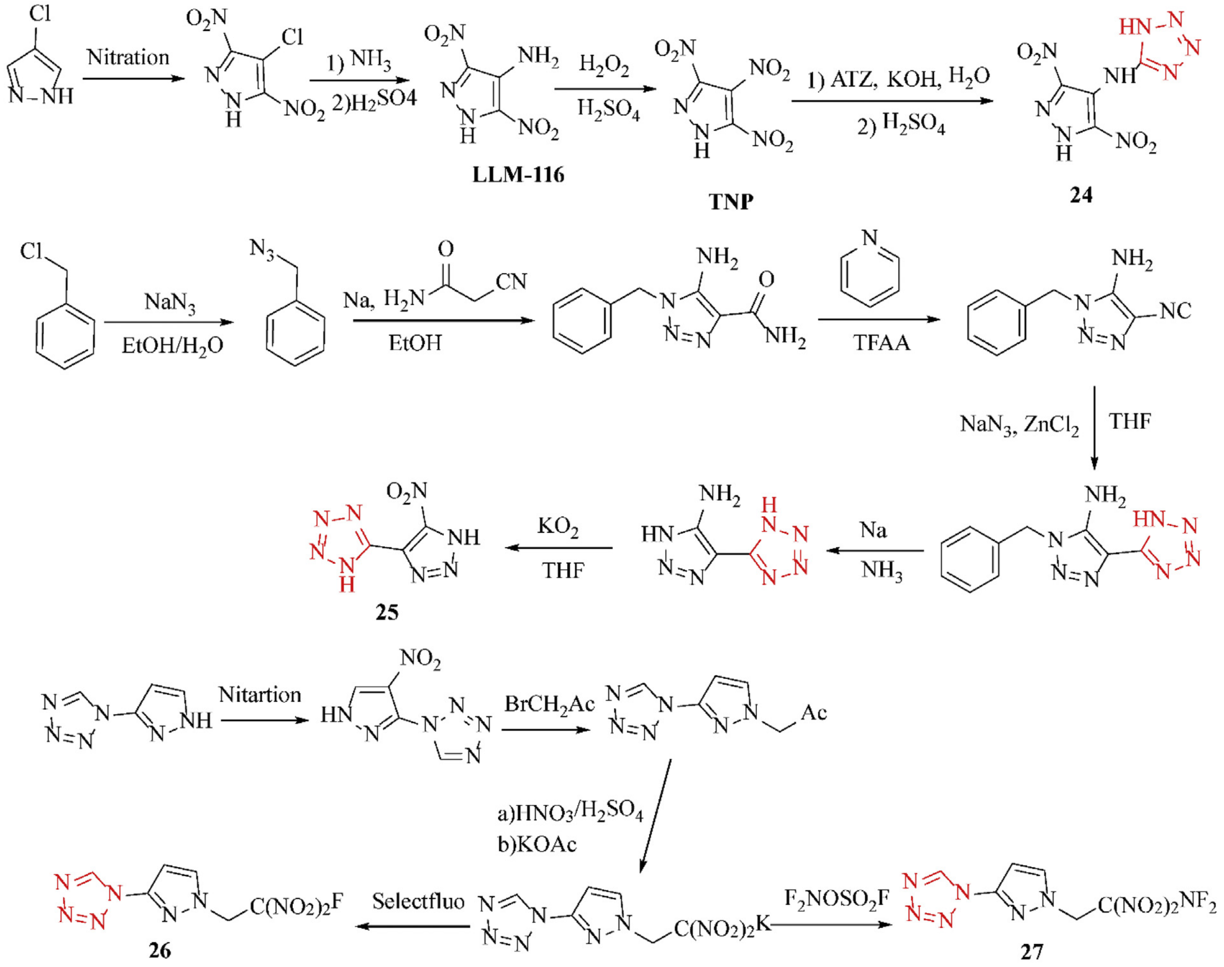
Scheme 3. Synthetic pathway of Poly-nitro groups containing tetrazole based compounds energetic compounds (20–23).

Table 3
Physiochemical and energetic properties of energetic compounds based on the tetrazole framework in a combination of nitro groups 24–34.

Compound	T_d /°C	d /(g·cm^{-3})	D /(m·s^{-1})	P /GPa	IS /J	FS /N	H_f /(kJ·mol^{-1})
24	279	1.86	9289	38.6	35	240	856.4
25	188	1.69	8251	26.3	4	108	516
26	111	1.81	8470	31	1.5	–	386
27	138	1.91	8990	36	1.6	–	589
28b-1	178	1.66 (1.63)	7432	20.4	–	–	403.9
28c-1	168	1.63 (1.56)	7305	19.5	–	–	408.7
28d-1	194	1.62	7243	19.1	–	–	392.9
28e-1	156	1.70 (1.62)	7274	19.9	–	–	302.7
28f-1	152	1.62	7268	19.7	–	–	287.4
28f-2	177	1.65 (1.64)	7432	21.0	–	–	322.4
28g-1	171	1.66 (1.65)	7442	21.1	–	–	293.7
28i-1	167	1.64	7142	18.9	–	–	654.3
28i-2	–	1.68	7812	21.9	–	–	628.0
29	181	1.87	9010	32.8	35	300	721.6
30	275	1.83	8499	26.7	30	>360	181.5
31	272	1.76	8257	25.9	30	360	407.7
32	163	1.82	8746	31.5	5	120	811.2
33	290	1.80	8434	27.2	>40	>360	446.5
34	169	1.81	8681	34.3	<2	–	499.5
TNT	295	1.65	7303	21.3	15	353	−59.3
TATB	360	1.94	8544	32.1	50	360	−154.2
RDX	210	1.80	8795	34.9	7.5	120	70.7
HMX	280	1.91	9144	39.2	7	120	74.8

ammonia to achieve the targeted compound 5-(5-amino-2H-1,2,3-triazol-4yl)-1H-tetrazole. Furthermore, the nitro group was introduced through potassium superoxide in tetrahydrofuran to yield compound 25. The compound 25 has a thermal decomposition temperature (188 °C) lower than standard HEDMs (Table 3). The detonation velocity was 8251 m/s and the detonation pressure was found 26.3 GPa, which was superior to TNT. Moreover, the HOF was 516 kJ/mol and it was sensitive towards impact and friction. Therefore, the prepared compound 25 was only nearby to TNT in a sense of energetic performance.

To enhance density, HOF, and thermal stability compounds 26 and 27 were intended to synthesize by adopting a unique method of combining the nitropyrazole unit and tetrazole ring. The synthesis of these compounds is elaborated in Scheme 4 [61]. Moreover, in these energetic compounds, a fluorine atom is incorporated in $C(NO_2)_2F$ and $C(NO_2)_2NF_2$ form to increase further energetic properties like density and detonation performance. The 1-(1H-pyrazol-3 (5)-yl)-1H-tetrazole was used as a precursor to incorporate $C(NO_2)_2F$ and $C(NO_2)_2NF_2$ groups to prepare energetic compounds with improved properties. The precursor 1-(1H-pyrazol-3 (5)-yl)-1H-tetrazole was nitrated to obtain 1, 4-nitropyrazole, which was further reacted with bromoacetone to generate acetonyl pyrazole and dinitromethyl intermediate which was consequently used to synthesized potassium 1 (dinitromethyl)-pyrazole salt after the treatment with KOAc. The salt was fluorinated by Selectfluor to attain efficiently fluorodinitromethyl product 26 in (82% yield). Further, the salt was converted to difluoroamino)dinitromethyl (27) with the help of F_2NOSO_2F. Associating densities of these compounds exposed that 27 has the advanced value (1.91 g/cm^3), greater than RDX, and comparable to HMX (Table 3). While the other compound 26 has a density near RDX. The HOFs values were positive in the range of 386 and 589 kJ/mol progressive than RDX due to high nitrogen contents. The detonation pressure and velocity were 31 & 36 GPa, and 8470 & 8990 m/s respectively. Hence, compound 27 has superior detonation properties to RDX. These compounds decomposed at 111 °C and 138 °C and their impact sensitivity were lies in the range of 1.5 J–1.6 J, tremendously inferior to standard HEDMs. Therefore, the only compound which exhibited good density, HOF, nitrogen



Scheme 4. Synthetic pathway of energetic compounds based on the tetrazole framework in a combination with nitro groups.

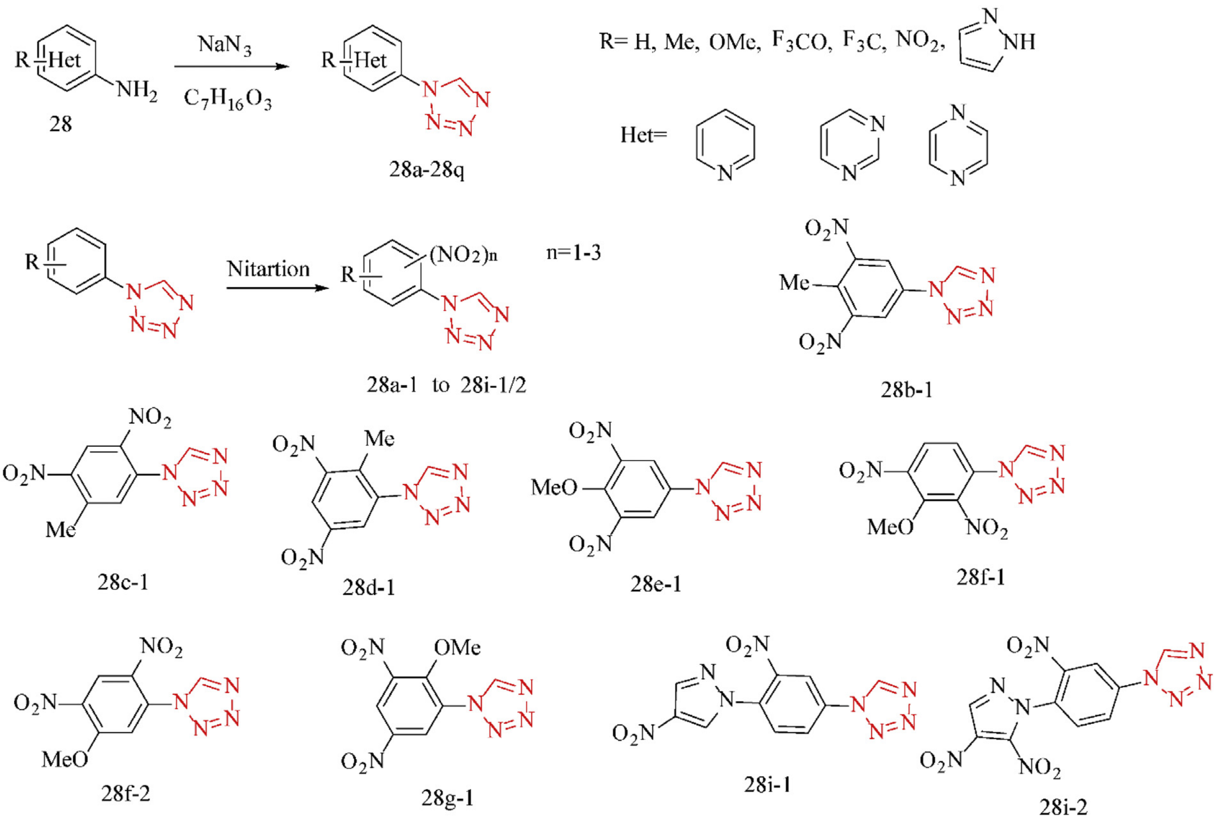
content, detonation performance, and ability to serve as a high-performance explosive was 27.

A large number of tetrazole-N-aryl/heteroaryl derivatives (28a-28q) were produced and further injected with energetic functional groups (-NO_2 and $-NHNO_2$) [57]. The synthetic route of tetrazole-*N*-aryl/heteroaryl derivatives and the further introduction of energetic functional groups are briefly described in Scheme 5. The conversion of amine moiety into tetrazole employing condensation and cycloaddition in the company of NaN_3 and triethyl orthoformate lead to the formation of tetrazole-N-aryl/heteroaryl derivatives (28a-28q). Further, the nitration of selected derivatives (from 28a-28r) with mixed acids (98% $HNO_3+H_2SO_4$) yielded a wide range of nitrated tetrazole-N-aryl/heteroaryl derivatives. Whereas, the synthesized compounds 28a-1 to 28i-1/2 behave as high performing explosive owing to their encouraging energetic properties.

The measured density of synthesized compounds was revealed 1.63–1.70 g/cm^3 noticeably imitating the increase from mononitro to dinitro substituted N-aryl-tetrazoles (Table 4). The detonation velocities and pressure were ranged from 7142 m/s to 7812 m/s and 18.9 GPa–21.9 GPa respectively, equivalent to TNT while lower than other references high-performance explosives. The prepared compounds were decomposed between 152 and 194 °C, presenting the thermal stability which was tempting for compound 28d-1 (194 °C). Furthermore, the synthesized compounds possess high positive HOFs due to the enrichment of nitrogen in the range of 287.4–654.3 kJ/mol essential factor for high-performance explosives. Hence, 28i-2 was found captivating energetic material due to retaining better detonation performance and density as compared to TNT.

7-nitro-3-(1H-tetrazol-5-yl)- [1,2,4]triazolo [5,1-c][1,2,4]triazin-4-amine was prepared using 3-nitro-1H-1,2,4-triazol-5-amine as precursor. The synthesis method of energetic compound 29 is represented in Scheme 6 [62]. The synthesis was easily achieved by the preparation of diazonium salts with malononitrile in the weak base solution followed by the introduction of a tetrazole ring using sodium azide in hydrochloric acid. The precursor 3-nitro-1H-1,2,4-triazol-5-amine was commercially available and retain a $-NO_2$ group. Therefore, the tetrazole moiety was introduced to enhance the energetic properties of compound 29. The impact and friction sensitivities are 35 J and 300 N respectively presenting its insensitive nature (Table 3). The detonation pressure was 32.8 GPa, detonation velocity was 9010 m/s, and density was 1.87 g/cm^3 higher than RDX. Furthermore, the calculated HOF was found 721.6 kJ/mol and thermal decomposition temperature of 181 °C. Thus, compound 29 exhibited less thermal stability, better density, HOF, and detonation performance than RDX.

The design of energetic compound 30 was the result of inspiration from FOX-7, which was prepared by utilizing 4,6-dichloro-5 nitropyrimidine as starting material in various steps as articulated in Scheme 6 [63,64]. The starting material was prepared through the reaction of 6-chloro-5-nitropyrimidin-4-amine and liquid



Scheme 5. Synthetic method of different nitro-tetrazole derivatives.

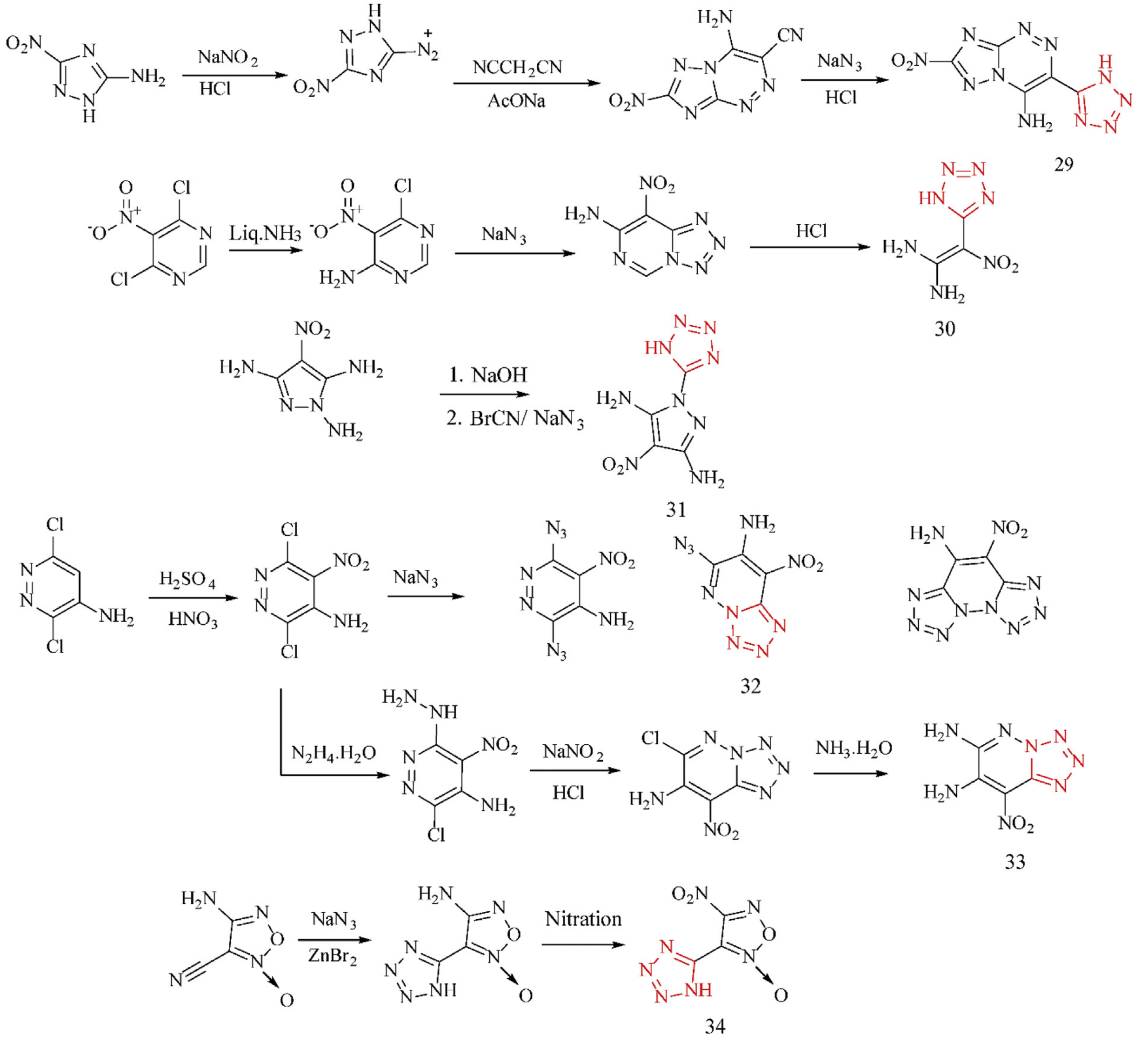
Table 4
Physiochemical and energetic properties of different Nitrato/Nitramino/Nitrimino-tetrazole energetic compounds (35–45).

Compound	T_d /°C	d /(g·cm^{-3})	D /(m·s^{-1})	P /GPa	IS /J	FS /N	H_f /(kJ·mol^{-1})
35	215	1.70	8062	26.2	<1	18	576
36	116	1.85	8776	34.2	<1	60	515
37	204	1.71	8187	24.9	15	240	476.2
38	159	1.81	8750	31.8	10	159	285.0
39	218	1.72	8213	25.2	18	360	462.8
40	240	2.18	10,011	52.2	1	<5	−112.4
41	116	1.66	8660	31.5	5	–	504.28
42	177	1.78	9141	33.6	18	180	923.3
43	186	1.74	8885	32.1	22	204	950.6
44	136	1.65	7824	23.09	39	360	463.0
45	170.81	1.801	9260	37.92	4.1	–	228.07
TNT	295	1.65	7303	21.3	15	353	−59.3
TATB	360	1.94	8544	32.1	50	360	−154.2
RDX	210	1.80	8795	34.9	7.5	120	70.7
HMX	280	1.91	9144	39.2	7	120	74.8
CL-20	210	2.04	9706	45.2	4	94	397.8

ammonia. Which was further reacted with sodium azide to attain 8-nitrotetrazolo [1,5-c]pyrimidin-7-amine followed the reaction with methanol HCl gas mixture to reach planned compound 30. The calculated density was found 1.83 g/cm^3 comparable to RDX and higher than TNT (Table 3). The compound 30 has good detonation velocity (8499 m/s) and detonation pressure (26.7 GPa) as compared to RDX and TNT, owing to the high density (1.83 g/cm^3) and positive HOF (181.5 kJ/mol). The impact and friction sensitivities (30 J and >360 N) were found acceptable and thermally stable up to the 275 °C. Therefore, Fox-7 like compound 30 can be used as a secondary explosive.

Keeping in view the importance of nitrogen-rich heterocycle such as tetrazole for the development of high performing explosive, compound 31 was designed and synthesized according to the method shown in Scheme 6 [65]. The sodium salt of precursor 3,5-diamino-4-nitropyrazole reacted with cyanogen azide to achieve the designed compound 31. The thermal stability up to 272 °C of the compound was superior to TNT and RDX as shown in Table 3. The calculated density was 1.76 g/cm^3 HOF was 407.7 kJ/mol. Owing to the reasonable density and HOF, the detonation velocity (8257 m/s) and pressure (25.9) GPa were also acceptable. Moreover, the impact and friction sensitivities were 30 J and >360 N respectively. Therefore, this compound with tuning properties of higher thermal stability, high detonation velocity, and low sensitivities was found interesting to use as high performing explosive. Furthermore, 1-((1H-tetrazol-5-yl)methyl)-1H-tetrazol-5-amine (Scheme 6) [66] was easily obtained after the reaction of 2-(5-amino-1H-tetrazol-1-yl)acetonitrile with sodium azide.

Another effort was done to attain the tetrazolo [1,5-b]pyridazine-compounds i.e. [6-azido-8-nitrotetrazolo [1,5b]pyridazine-7-amine (32) and 8-nitrotetrazolo [1,5-b]pyridazine-6,7-diamine (33) as shown in Scheme 6 [67]. The synthesized compounds 32 and 33 have thermal decomposition temperature 163 °C and 290 °C and densities 1.82 g/cm^3 and 1.80 g/cm^3 (Table 3). These results indicated that densities were comparable to RDX, while thermal stability was greater than RDX in the case of 33. The thermal stability of 32 was very low due to the presence of the azido group. Because these compounds have an excess of N—N or C—N bonds, therefore the HOFs were positive (811.2 kJ/mol and 446.2 kJ/mol). Whereas, the detonation pressure (31.5 GPa and 27.2 GPa) and velocity (8746 m/s and 8446 m/s) were relatively lower than reference high-performance explosive except for TNT. However, these compounds synthesized by a simple technique, but due to

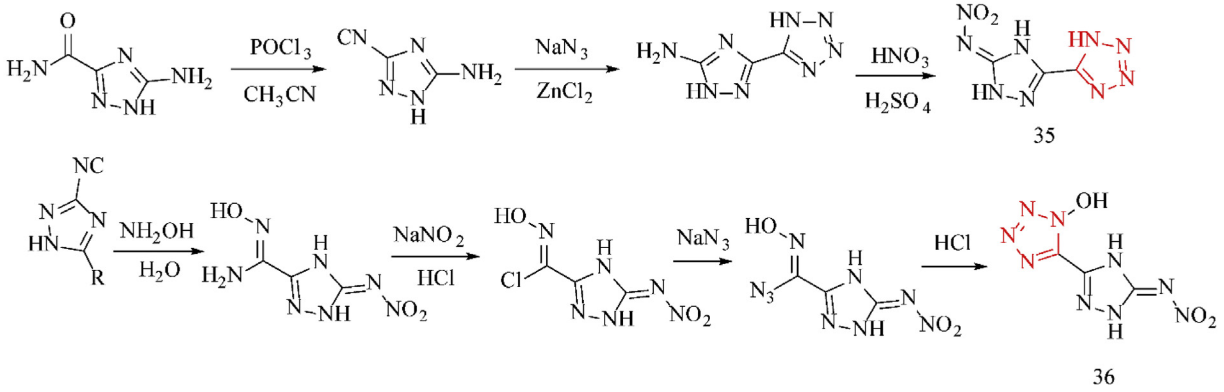


Scheme 6. Synthetic method of different nitro-tetrazole derivatives.

high detonation performance, compound 32 predicated as a primary explosive, while good thermal stability, sensitivity, and detonation performance of compound 33 making it suitable as a secondary explosive. The starting material 3,6-dichloropyridazin-4-amine was nitrated with mixed acids (100% HNO_3+H_2SO_4) to obtain 3,6-dichloropyridazin-4-amine. The intermediate 3,6-dichloropyridazin-4-amine was further treated with sodium azide to yield 32 interestingly in azido-tetrazole form instead of a mixture of three tautomers (diazide, azide-tetrazole, and ditetrazole). For the synthesis of compound 33, in the first step hydrazine monohydrate was reacted with 3,6-dichloropyridazin-4-amine to obtain 3-chloro-6-hydrazinyl-5-nitropyridazin-4-amine. Which was further undergo two-step reactions, with sodium nitrite in dilute HCl and aqueous ammonia resultantly the formation of 33. The purpose of the synthesis of 4-nitro-3-(5-tetrazole)furoxan (HTNF, 34) was with furazan ring-substituted tetrazole to attain high thermal stability, density, and HOF [68]. The synthesis was started from 4-amino-3-cyanofuroxan as shown in Scheme 6. The 4-amino-3-cyanofuroxan was reacted with sodium azide in the presence of zinc bromide to develop the tetrazole ring [69], further the reaction continue for nitration and produced HTNF (34). The decomposition temperature of HNTF (34) was 169 °C assimilated into Table 3. Moreover, the calculated density was 1.81 g/cm^3 which was comparable to RDX. The high HOF (499.5 kJ/mol) detonation pressure and velocity (34.3 GPa and 8681 m/s) made this compound to be used as high performance explosive.

2.3. *Nitrato/nitramino/nitrimino -tetrazole compounds*

The heterocyclic compounds comprise alkyl and alkoxy principally nitrato/nitramino/nitrimino-tetrazole have gained enormous attention among chemical researchers for the production of high performing explosive. Therefore, nitrimino containing energetic compounds 35, and 36 were designed and synthesized to achieve the appropriate energetic properties as referred to Scheme 7 [70]. The raw material 5-amino-1H-1,2,4-triazole-3-carbonitrile was used to yield the 5-(1,2,4-triazol-C-yl)tetrazoles (35) and 5- (1,2,4-triazol-C-yl)tetrazol-1-oles (36) [71,72]. 3-isocyano-1H-1,2,4-triazol-5-amine was undergone cycloaddition in the presence of sodium azide and $ZnCl_2$, to yield 3-(1H-tetrazol-5-yl)-1H-1,2,4-triazol-5-amine. Subsequently, the reaction continues to nitration to harvest compound 35 containing nitrimino energetic groups.



Scheme 7. Synthesis of Nitrimino-tetrazole energetic compounds 35 and 36.

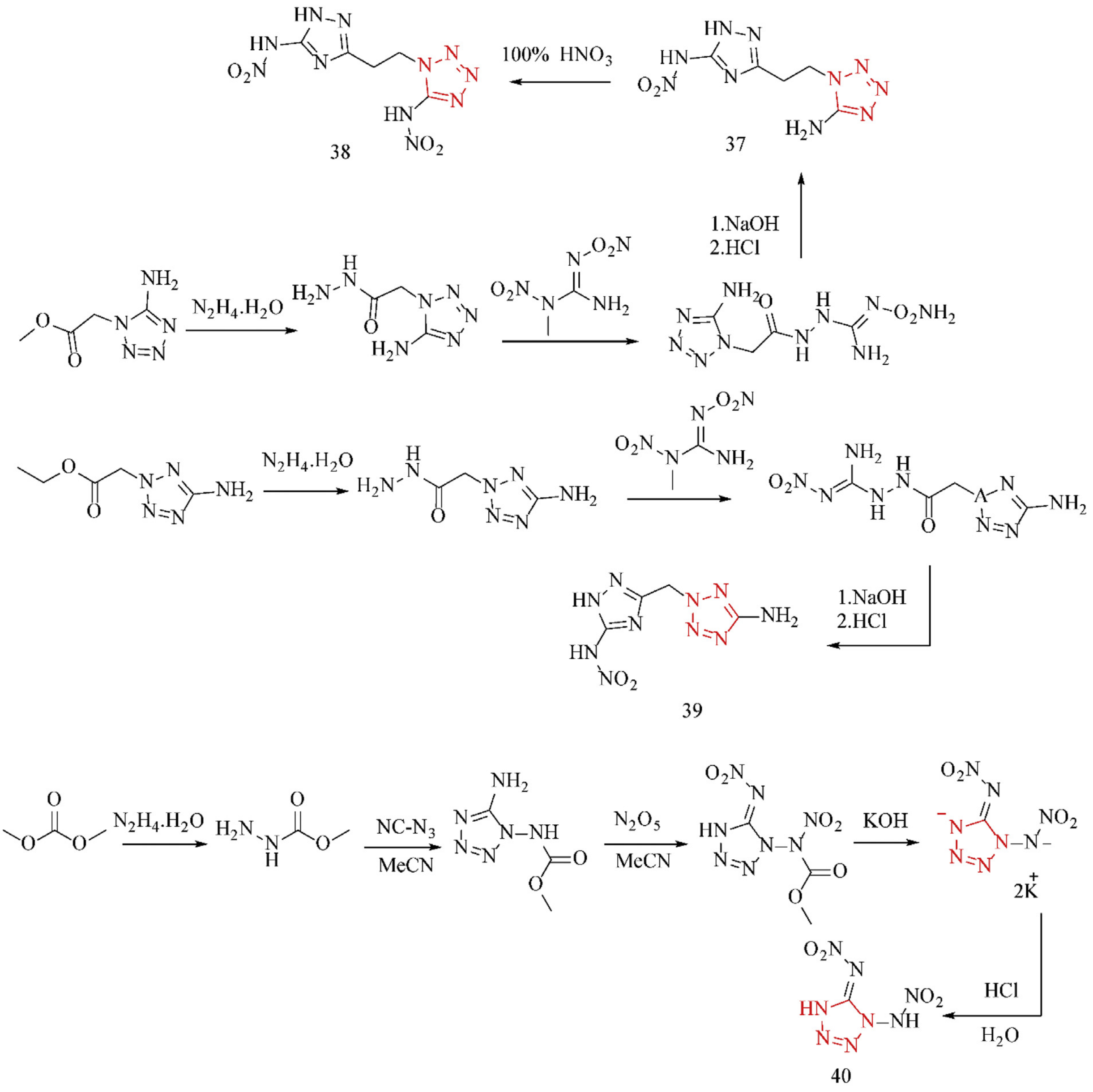
However, while preparing compound 35 the energetic compounds introduced first and then undergo cyclization in numerous step reactions. The thermal decomposition temperature was 215 °C and 116 °C respectively for these prepared compounds (35 and 36) as represented in Table 4. The calculated HOFs were superior to RDX which was 576 kJ/mol and 515 kJ/mol respectively. Moreover, the calculated detonation pressure of compounds 35, and 36 was 26.2 GPa and 34.2 GPa and detonation velocities were 8062 m/s and 8776 m/s respectively. The impact (<1, and <1 J) and friction (18, and 60 N) sensitivities were not very reasonable. Therefore, from theses designed compounds the 36 demonstrated superlative energetic performance in terms of detonation performance, HOF, and density in the range of RDX.

Thus, energetic compounds 37, 38, and 39 were also planned according to this approach (Scheme 8) [73]. The starting materials (methyl-2-(5-amino-1H-tetrazol-1-yl) acetate and ethyl-2-(5-amino-2H-tetrazol-2-yl)acetate respectively) were different for the synthesis of these compounds. The raw materials were reacted with hydrazine monohydrate, N-methyl-N-nitroso-N′-nitroguanidine, and finally refluxing in sodium hydroxide solution by acidifying with concentrated hydrochloric acid to produce 37 and 39. Furthermore, the nitration of compound 37 by concentrated HNO_3 leads to the formation of energetic compound 38. The densities of prepared compounds (37, 38, and 39) were found 1.71, 1.81, and 1.72 g/cm^3 respectively as given away in Table 4. The obtained density and HOF of compound 38 was high (1.81 g/cm^3) among all and comparable to RDX as well. The disintegration temperature was 204, 159, and 218 °C, which is not appropriate in the case of compound 37 and 39. The impact (15, 10, and 18 J) and friction (240, 159, and 360 N) sensitivities of all the compounds were found acceptable. Furthermore, the detonation velocities were 8187, 8750, and 8213 m/s and detonation pressures were 24.9, 31.8, and 25.2 GPa respectively for compounds 37, 38, and 39. The detonation velocity of compounds 38 was 8750 m/s which is comparable to RDX. Whereas, the detonation pressure was not higher than RDX for these compounds. The high HOF, density, and detonation performance made compound 38 as promising high performance explosive.

The synthesis of nitramino tetrazole compound 40 was accomplished over dimethyl carbonate, which was promoted to react with hydrazine hydrate to yield methyl carbazate as articulated in Scheme 8 [74]. Further, the methyl carbazate was treated with cyanogen azide to provide N-methoxycarbonyl 1,5-diaminotetrazole. The product N-methoxycarbonyl 1,5-diaminotetrazole was additionally nitrated (N_2O_5 in methyl cyanide) and decomposed in the KOH solution. Finally, the potassium salt undergoes acidification by aqueous hydrochloric to yield compound 40. The compound 40 possessed a thermal decomposition temperature of 240 °C, calculated detonation velocity of 10,011 m/s· and pressure of 52.2 GPa respectively, as shown in Table 4. However, compounds 40 was found highly sensitive towards impact and friction due to which it can be used as a primary explosive. The 1-methoxy-5-aminotetrazole (41) was obtained after the reaction of cyanogen azide and methoxy amine and subsequently neutralization with NaOH, and nitration via 100% HNO_3 as represented in Scheme 9 [21]. The synthesized compound 41 was highly sensitive as indicated by the physiochemical and energetic properties given in Table 4. This compound has less thermal stability (116 °C) and having low density (1.66 g/cm^3) as compared to standard high performing explosive. However, the detonation velocity was 8660 m/s and the detonation pressure was 31.5 GPa which was closer to RDX, making it a considerable high performing explosive.

Researchers found that the nitrogen-rich heterocyclic skeletons were an effective and adequate way to enhance the abilities of new high-performance explosives [75]. For this purpose, the C—N hetero-aromatic compounds like triazole and tetrazole are unique classes due to their brilliant energetic strengths with great HOF and high thermal stability resulting from their aromaticity [76,77]. The synthesis of long catenated nitrogen atom chains having heterocyclic compounds might be an interesting approach to expand the energetic properties [78]. In this regard, the research group of Guangbin Cheng synthesized the long catenated nitrogen atoms inclosing tetrazole compound (1H-tetrazol-1-yl)-4H-1,2,4-triazole-3,4-diamine and it's nitro group derivatives as represented in Scheme 9 [54]. The starting reagent 4-amino-3-hydrazino-1,2,4-triazolelium chloride experiences cyclization with sodium azide and triethyl orthoformate to yield compound (1H-tetrazol-1-yl)-4H-1,2,4-triazole-3,4-diamine. Further, the compounds (nitramino) 42 and (nitro) 43 were obtained by the nitration of (1H-tetrazol-1-yl)-4H-1,2,4-triazole-3,4-diamine with fuming HNO_3 and a mixture of nitration acids (100% HNO_3 + 98% H_2SO_4) respectively in good yield. The compounds 42, and 43 exhibited thermal stability of 177 °C and 186 °C and densities of 1.78 g/cm^3 and 1.72 g/cm^3 respectively as listed in Table 4. The calculated densities were only advanced than TNT. The HOF was positive for both compounds (42 and 43) which was 923.3 and 950.6 kJ/mol respectively. The calculated detonation performance (velocity; 9141, and 8885 m/s and pressure; 33.6, and 32.1 GPa) was found closer or higher than RDX. The synthesized compounds were found sensitive to impact and friction. Additionally, these compounds have gained their importance to be used as high-performance explosives due to their high HOFs and detonation performances.

Nitramino and tetrazole bearing energetic compound 44 was



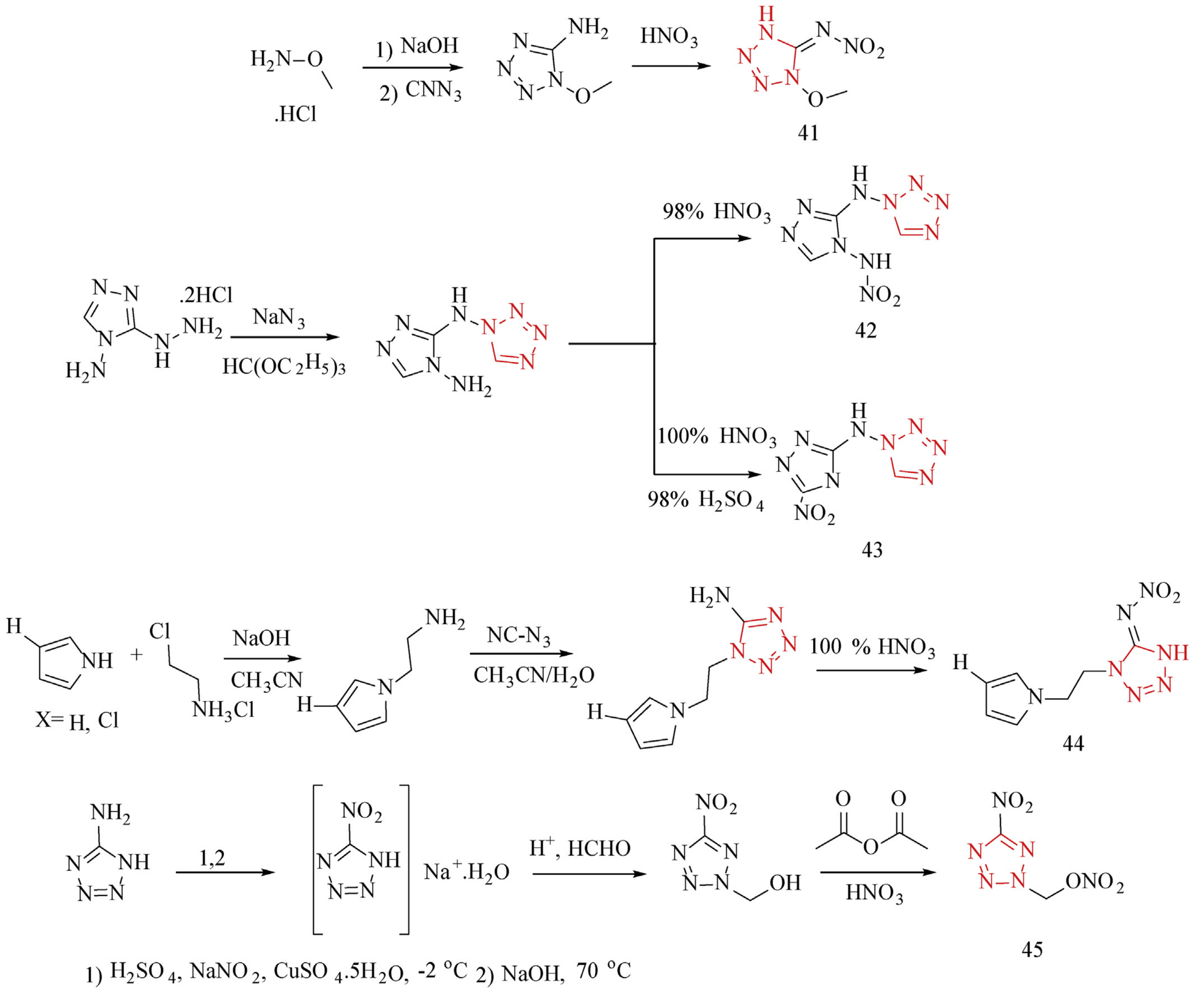
Scheme 8. Synthesis of Nitrimino/Nitramino -tetrazole energetic compounds 37–40.

synthesized by Shreeve's group as demonstrated in Scheme 8 [53]. The starting reaction was conducted between 2-chloroethylamine and pyrazole, in the presence of NaOH to yield 2-(1H-pyrrol-1-yl) ethan-1-amine, which was further reacted with cyanogen azide to carry out compound 1-(2-(1H-pyrrol-1-yl)ethyl)-1H-tetrazol-5-amine, N,N-ethylene bridge un-substituted pyrazole, and amino-tetrazole. The reaction further continues and the former product was reacted with 100% nitric acid to attain the compound 44. Unfortunately, the energetic properties of this synthesized compound are only better than TNT.

The compound 5-nitro-2-nitratomethyl-1,2,3,4-tetrazole (45) was prepared by nitration of 5-nitro-2-hydroxymethyl-tetrazole by nitric acid and acetic anhydride as described in Scheme 9 [79]. The 5-nitro-2-hydroxymethyl-tetrazole compound was attained after the reaction of 5-nitrotetrazole sodium salt with formaldehyde in the presence of a strong acid like H_2SO_4. The compound 45 exhibited high density, detonation performance, and HOF, which were 1.80 g/cm^3, 9260 m/s (detonation velocity) 37.92 GPa (detonation pressure) and 228.07 kJ/mol (Table 4). Therefore, the energetic performance was better than TNT, RDX, and comparable to HMX. However, the compound has low sensitivity towards impact (4.1 J) and less thermal decomposition temperature (170.81 °C) as compared to reference energetic materials. Thus, the importance of this energetic compound is due to its high density, HOF, and detonation performance which make it an appropriate high performance explosive.

2.4. Bridged/bis/di tetrazole and nitro groups containing energetic compounds

Bridged/Bis/Di tetrazole connecter linkage is very important to obtain high-performance explosives [80]. 3,6-dinitropyrazolo [4,3-c]pyrazole (DNPP) was prepared through a series of reaction steps followed by the literature method, which was further used to synthesized 3,6-dinitro-1,4-di (1H-tetrazol-5-yl)-pyrazolo [4,3-c] pyrazole (DNTPP (46)) as shown in Scheme 10 [81,82]. The

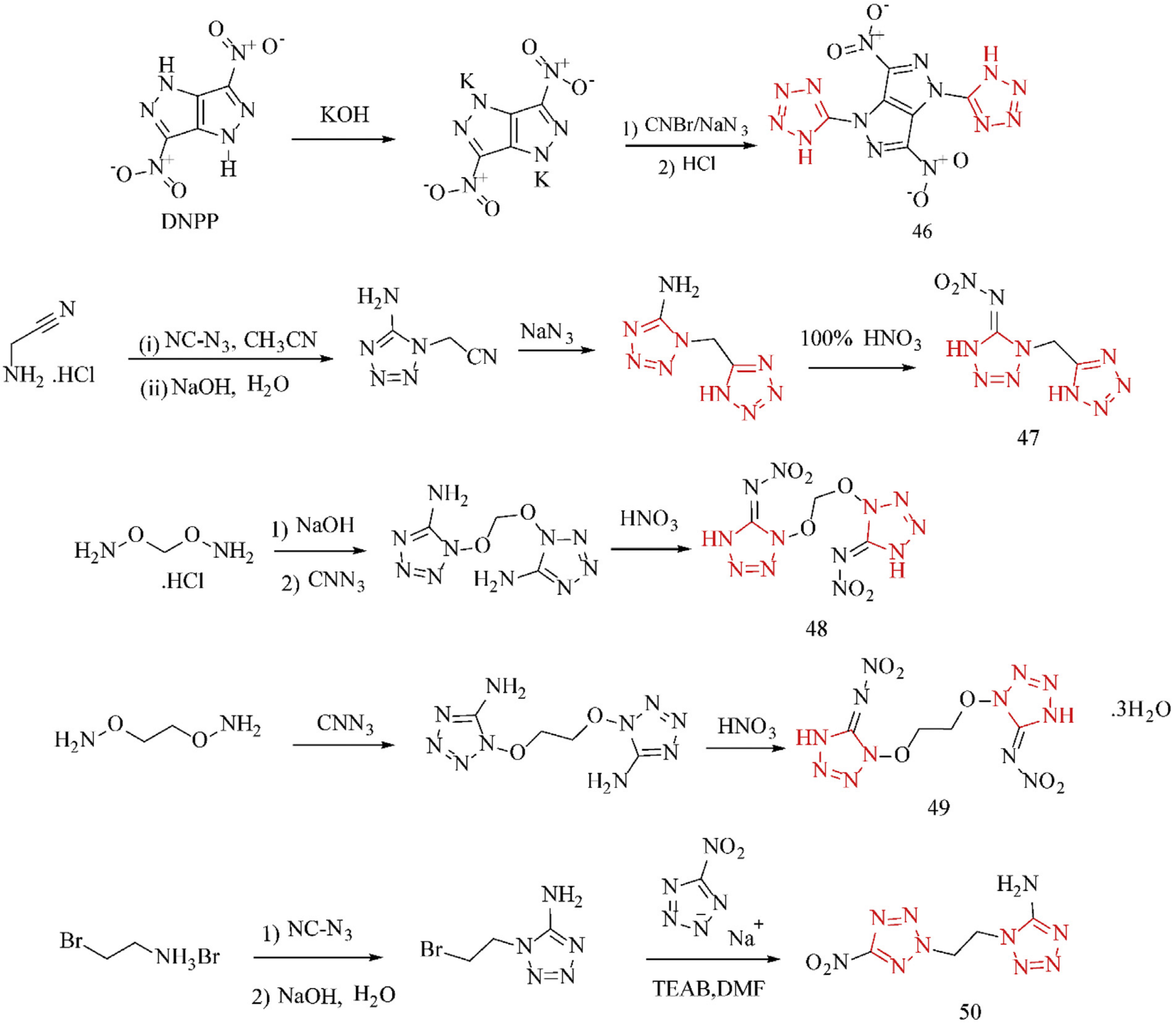


Scheme 9. Synthesis of Nitrato/Nitramino/Nitrimino -tetrazole compounds energetic compounds 41–45.

potassium salt of DNPP was prepared through the acid-base neutralization method in the presence of KOH. In this potassium salt of the DNPP, the tetrazole moiety was introduced via *in-situ* produced cyanogen azide (a mixture of sodium azide and cyanogen bromide) to achieved the targeted compound 46. The compound 46 possesses good thermal stability of 281 °C (Table 5). The detonation velocity was 8721 m/s and detonation pressure was 30.9 GPa, which is not higher than RDX. However, the compound was insensitive towards impact and friction, exhibited high HOF (1111.5 kJ/mol), density (1.79 g/cm^3), and thermal stability (281 °C).

The nitramino functional group was introduced to offer efficient energetic properties by the reaction of 1-((1H-tetrazol-5-yl) methyl)-1H-tetrazol-5-amine with conc. HNO_3 to finalized compound 47 [83]. The physiochemical and energetic properties of compound 47 are represented in Table 5. The nitrogen-rich framework (tetrazole) and the nitro group-containing compounds 47 have a decomposition temperature of 178 °C and density was 1.76 g/cm^3. The calculated HOF was found 615.9 kJ/mol higher than TNT and RDX. The compound 47 has adequate density and HOF, therefore the detonation performance (velocity and pressure) was promising (8652 m/s and 29.6 GPa). Moreover, the impact (>12) and friction (160 J) sensitivities were found better in comparison to RDX. Thus, the energetic compound 47 can be used as a secondary explosive.

The *oxy* nitroiminotetrazoles, derivatives of nitroiminotetrazole (48 and 49) was synthesized to reach good physical and energetic properties as presented in Scheme 10 [84,85]. The reaction of cyanogen azide and methoxy amine and subsequently neutralization with NaOH, and nitration via 100% HNO_3 used to obtain the energetic compounds 48 and 49. The produced compounds (48 and 49) were found thermally less stable (157, and 134 °C respectively) in comparison to standard high-performance explosives. The calculated densities of these compounds were 1.90, and 1.81 g/cm^3. The density of compound 48 was higher (1.90 g/cm^3), which was reachable to RDX, HMX, and TATB. These compounds were sensitive in comparison to the high performance explosive as the sensitivity range was 1–1.5 J. Moreover, the detonation pressure and velocity were 46.7, and 38.4 GPa and 9867, and 9200 m/s respectively, reachable to the standard high performance explosive. Therefore, compound 48 exhibited high detonation performance (velocity 9867 m/s and pressure 46.7 GPa) which is greater than HMX. Thus, although these compounds (48 and 49) were exhibited less thermal



Scheme 10. Synthetic routes to Bridged/Bis/Di tetrazole and nitro groups containing energetic compounds 46–50.

Table 5
Physiochemical and energetic properties of different Bridged/Bis/Di tetrazole and nitro groups containing energetic compounds (46–50).

Compound	T_d /°C	d /(g·cm^{-3})	D /(m·s^{-1})	P /GPa	IS /J	FS /N	H_f /(kJ·mol^{-1})
46	281	1.79	8721	30.9	15	192	1111.5
47	178	1.76	8652	29.6	>12	160	615.9
48	157	1.90	9867	46.7	1	–	1088.82
49	134	1.81	9200	38.4	1.5	–	1291.63
50	234	1.70	8279	25.6	40	>360	559.8
TNT	295	1.65	7303	21.3	15	353	−59.3
TATB	360	1.94	8544	32.1	50	360	−154.2
RDX	210	1.80	8795	34.9	7.5	120	70.7
HMX	280	1.91	9144	39.2	7	120	74.8
CL-20	210	2.04	9706	45.2	4	94	397.8

stability and high impact sensitivities, they possess excellent detonation performance and can be used as high-performance explosives. In Scheme 10 the synthesis system of unsymmetrical tetrazole-based N,N′-ethylene-bridged energetic compound 50 was also particularized [86]. The reaction of bromoethylamine hydrobromide with cyanogen azide in the presence of sodium hydroxide yielded initiating compound 1-(2-Bromoethyl)-5-aminotetrazole. The reaction of starting material 1-(2-Bromoethyl)-5-aminotetrazole in the presence of TEAB in DMF with the sodium salt of 5-nitrotetrazole yielded the targeted compound 50. The prepared compound 50 was expected to rich in energetic properties such as high thermal stability, density, HOF, and detonation performance due to nitrogen augment heterocyclic moieties [87]. Therefore, the energetic and physicochemical properties are given in Table 5, which shows that the thermal decomposition temperature was 234 °C. The density (1.70 g/cm^3), detonation velocity

(8279 m/s), detonation pressure (25.6 GPa) were higher than TNT. However, insensitivity towards impact and friction of the prepared compound and high thermal stability makes it useful as high performing explosive.

3. Conclusion and future trends

Recently, the design and synthesis of modern high-performing explosives especially heterocyclic compounds combined with energetic substituents possessing high energy, density, and detonation properties attained prevalent attention as the potential replacement for the traditional energetic materials. Tetrazole a heterocyclic moiety is considered an important precursor for the development of a wide range of energetic compounds due to its unique properties and practical significance. The ideal properties for the high performing explosives are high density, thermal stability, detonation performance (velocity and pressure), positive heat of formation (HOF), insensitivity, and environmentally friendly nature. Therefore, to achieve these properties, tetrazole moiety combined with different energetic functional groups such as nitro ($-NO_2$), nitrato ($-ONO_2$), nitrimino ($-NNO_2$), and nitramino ($-NH-NO_2$).

In this review, the current developments in the field of tetrazole based energetic compounds containing energetic functional groups ($-NO_2$, $-ONO_2$, $-NNO_2$, and $-NH-NO_2$) were designed and synthesized are discussed since 2010, which can be considered as a potential replacement for the traditionally used compounds such as RDX or HMX. Ideally, the detonation velocities of new compounds should be greater than 8500 m/s, thermal stability up to 200 °C, impact sensitivity, and friction sensitivities should be greater than 7 J and 120 N respectively. Moreover, the products of decomposition should be environmentally friendly, the yield of reaction should be high and associated with low-cost synthesis. Among all of the nitro-tetrazole energetic compounds discussed here many exhibit physical and detonation properties competitive with TNT or TATB, and numerous compounds (1, 2, 5, 12, 20, 27, 29, 30, 34, 36, 38, 41, 42, 43, and 49) possess similar or even improved detonation properties as compared to RDX. The thermal stabilities of the compounds 15, 18, 23, 24, 30, 31, 33, 35, and 50 are advanced than RDX. While looking at densities of compounds 2, 3, 5, 12, 23, 24, 29, 30, 32, 33, 38, 41, 45, and 49 found promising to replace RDX. Whereas, the detonation properties (4, 24, 45, and 48) and densities of (4, 27, and 48) some compounds are even better than HMX. The compound 40 demonstrated promising detonation performance and density than CL-20 but it exhibits high sensitivities towards impact and friction therefore it can be used as a primary explosive. However, this is worth noting that the poly-nitro tetrazole energetic compounds such as 1–13 enjoyed greater detonation performance and density as compared to the fewer number of these energetic groups containing compounds. Although these properties of high detonation performance and densities are achieved on the contrary to low thermal stability and high sensitivity towards impact and friction. Hence, the poly-nitro tetrazole compounds are evidenced for enhancement of densities and detonation performance whereas, the less number favor high disintegration temperature and insensitivities towards impact and friction. Therefore, this strategy to attain the molecular design of new high performing explosives with balanced physiochemical and energetic properties in the future becomes more challenging and demanding.

Furthermore, there are some areas demanding improvement for the further synthesis of tetrazole based energetic compounds containing energetic functional groups ($-NO_2$, $-ONO_2$, $-NNO_2$, and $-NH-NO_2$). First, traditional nitration is generally used in the synthesis of these energetic compounds which does not meet the requirements of modern green chemistry. It is necessary to find out the appropriate green nitrating agents and catalysts in the future synthesis process. Second, the synthesis of many nitro-tetrazole energetic compounds requires several steps, leading to a low yield and high cost. Therefore, it is vital to search for an efficient route when preparing new high performing explosives.

Declaration of competing interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dt.2021.02.002.

References

[1] Liu Z, Lu T, Xue F, Nie H, Withers R, Studer A, Kremer F, Narayanan N, Dong X, Yu D. Lead-free (Ag, K) NbO3 materials for high-performance explosive energy conversion. Sci Adv 2020;6(21):eaba0367.

[2] Hartdegen V, Klapötke TM, Sproll SM. Tetrazole-5-carboxylic acid based salts of earth alkali and transition metal cations. Inorg Chem 2009;48(19):9549–56.

[3] Klapötke TM, Stein M, Stierstorfer J. Salts of 1H-Tetrazole—Synthesis, characterization and properties. Z Anorg Allg Chem 2008;634(10):1711–23.

[4] Wang R, Guo Y, Zeng Z, Shreeve JM. Nitrogen-rich nitroguanidyl-functionalized tetrazolate energetic salts. Chem Commun 2009;(19):2697–9.

[5] Zhang J, Yin P, Pan G, Wang Z, Zhang J, Mitchell LA, Parrish DA, Shreeve JM. 5-(4-Azidofurazan-3-yl)-1-hydroxytetrazole and its derivatives: from green primary to secondary explosives. New J Chem 2019;43(32):12684–9.

[6] Gospodinov I, Hermann T, Klapötke TM, Stierstorfer J. *Energetic Compounds Based on 3, 4-Bis (4-nitramino-1, 2, 5-oxadiazol-3-yl)-1, 2, 5-furoxan (BNAFF).* Propellants, Explosives. Pyrotechnics 2018;43(4):355–63.

[7] Gao H, Shreeve JM. Azole-based energetic salts. Chem Rev 2011;111(11):7377–436.

[8] Li Y, Wang B, Chang P, Hu J, Chen T, Wang Y, Wang B. Novel catenated N 6 energetic compounds based on substituted 1, 2, 4-triazoles: synthesis, structures and properties. RSC Adv 2018;8(25):13755–63.

[9] Yin P, Zhang J, He C, Parrish DA, Shreeve JM. Polynitro-substituted pyrazoles and triazoles as potential energetic materials and oxidizers. J Mater Chem 2014;2(9):3200–8.

[10] Jiao F, Xiong Y, Li H, Zhang C. Alleviating the energy & safety contradiction to construct new low sensitivity and highly energetic materials through crystal engineering. CrystEngComm 2018;20(13):1757–68.

[11] Tang Y, He C, Imler GH, Parrish DA, Shreeve JM. Aminonitro groups surrounding a fused pyrazolotriazine ring: a superior thermally stable and insensitive energetic material. ACS Appl Energy Mater 2019;2(3):2263–7.

[12] Zhang M, Gao H, Li C, Fu W, Tang L, Zhou Z. Towards improved explosives with a high performance: N-(3, 5-dinitro-1 H-pyrazol-4-yl)-1 H-tetrazol-5-amine and its salts. J Mater Chem 2017;5(4):1769–77.

[13] Fried LE, Manaa MR, Pagoria PF, Simpson RL. Design and synthesis of energetic materials. Annu Rev Mater Res 2001;31(1):291–321.

[14] Bolton O, Matzger AJ. Improved stability and smart-material functionality realized in an energetic cocrystal. Angew Chem Int Ed 2011;50(38):8960–3.

[15] Fischer D, Klapötke TM, Reymann M, Stierstorfer J, Völkl MB. Energetic alliance of tetrazole-1-oxides and 1, 2, 5-oxadiazoles. New J Chem 2015;39(3):1619–27.

[16] Yin P, Zhang Q, Shreeve JM. Dancing with energetic nitrogen atoms: versatile N-functionalization strategies for N-heterocyclic frameworks in high energy density materials. Accounts Chem Res 2016;49(1):4–16.

[17] Wang P, Xu Y, Lin Q, Lu M. Recent advances in the syntheses and properties of polynitrogen pentazolate anion cyclo-N 5− and its derivatives. Chem Soc Rev 2018;47(20):7522–38.

[18] Gao H, Zhang Q, Shreeve JM. Fused heterocycle-based energetic materials (2012–2019). J Mater Chem 2020;8(8):4193–216.

[19] Wang Q, Shao Y, Lu M. Azo1, 3, 4-oxadiazole as a novel building block to design high-performance energetic materials. Cryst Growth Des 2019;19(2):839–44.

[20] Zhang C. Origins of the energy and safety of energetic materials and of the energy & safety contradiction. Propellants, Explos Pyrotech 2018;43(9):855–6.

[21] Joo YH, Shreeve JM. High-density energetic mono-or bis (oxy)-5-

nitroiminotetrazoles. Angew Chem 2010;122(40):7478–81.

[22] Xu Z, Cheng G, Zhu S, Lin Q, Yang H. Nitrogen-rich salts based on the combination of 1, 2, 4-triazole and 1, 2, 3-triazole rings: a facile strategy for fine tuning energetic properties. J Mater Chem 2018;6(5):2239–48.

[23] Xue Q, Bi F-q, Zhang J-l, Wang Z-j, Zhai L-j, Huo H, Wang B-z, Zhang S-y. A family of energetic materials based on 1, 2, 4-oxadiazole and 1, 2, 5-oxadiazole backbones with low insensitivity and good detonation performance. Front Chem 2020;7:942.

[24] Badgujar D, Talawar M, Zarko V, Mahulikar PP. Recent advances in safe synthesis of energetic materials: an overview. Combust Explos Shock Waves 2019;55(3):245–57.

[25] Gorn MV, Gritsan NP, Goldsmith CF, Kiselev VG. Thermal stability of bis-tetrazole and bis-triazole derivatives with long catenated nitrogen chains: quantitative insights from high-level quantum chemical calculations. J Phys Chem 2020;124(38):7665–77.

[26] Fischer D, Klapötke TM, Piercey DG, Stierstorfer J. Synthesis of 5-aminotetrazole-1 N-oxide and its azo derivative: a key Step in the Development of new energetic materials. Chem A Eur J 2013;19(14):4602–13.

[27] Gálvez-Ruiz JC, Holl G, Karaghiosoff K, Klapötke TM, Löhnwitz K, Mayer P, Nöth H, Polborn K, Rohbogner CJ, Suter M. Derivatives of 1, 5-diamino-1 H-tetrazole: a new family of energetic heterocyclic-based salts. Inorg Chem 2005;44(12):4237–53.

[28] Singh RP, Verma RD, Meshri DT, Shreeve JM. Energetic nitrogen-rich salts and ionic liquids. Angew Chem Int Ed 2006;45(22):3584–601.

[29] Aureggi V, Sedelmeier G. 1, 3-Dipolar cycloaddition: click chemistry for the synthesis of 5-substituted tetrazoles from organoaluminum azides and nitriles. Angew Chem Int Ed 2007;46(44):8440–4.

[30] Li C, Liang L, Wang K, Bian C, Zhang J, Zhou Z. Polynitro-substituted bispyrazoles: a new family of high-performance energetic materials. J Mater Chem 2014;2(42):18097–105.

[31] Sun M, Yin Y, Pang Z. Predicted new structures of polymeric nitrogen under 100–600 GPa. Comput Mater Sci 2015;98:399–404.

[32] United Nations. Committee of experts on the transport of dangerous goods. *Recommendations on the transport of dangerous goods*: model regulations, vol. 1. United Nations Publications; 2009.

[33] Sućeska M. EXPLO5, version 6.01. Zagreb, Croatia. Brodarski Institute; 2013.

[34] Wang Q, Pang F, Wang G, Huang J, Nie F, Chen F-X. Pentazadiene: a high-nitrogen linkage in energetic materials. Chem Commun 2017;53(15):2327–30.

[35] Li X, Wang C, Li H, Nie F, Yin H, Chen F-X. Bishydrobis (tetrazol-1-yl) borate (BTB) based energetic ionic liquids with high density and energy capacity as hypergolic fuels. J Mater Chem 2017;5(30):15525–8.

[36] Klapötke TM, Schmid PC, Schnell S, Stierstorfer J. Thermal stabilization of energetic materials by the aromatic nitrogen-rich 4, 4′, 5, 5′-tetraamino-3, 3′-bi-1, 2, 4-triazolium cation. J Mater Chem 2015;3(6):2658–68.

[37] Brinck T. Introduction to green energetic materials. Wiley Online Library; 2014.

[38] Kofman T, Kartseva GY, Glazkova EY. 5-substituted 3-nitro-1-trinitromethyl-1, 2, 4-triazoles. Russ J Org Chem 2008;44(6):870–3.

[39] Klapötke TM, Krumm B, Scharf R. Oxalyl chloride and hydrazide based energetic polynitro derivatives. Eur J Inorg Chem 2016;2016:3086–93.

[40] Zhao X, Li S, Wang Y, Li Y, Zhao F, Pang S. Design and synthesis of energetic materials towards high density and positive oxygen balance by N-dinitromethyl functionalization of nitroazoles. J Mater Chem 2016;4(15):5495–504.

[41] Zhao XX, Li SH, Wang Y, Li YC, Zhao FQ, Pang SP. Design and synthesis of energetic materials towards high density and positive oxygen balance by N-dinitromethyl functionalization of nitroazoles. J Mater Chem 2016;4(15):5495–504.

[42] Fischer N, Karaghiosoff K, Klapötke TM, Stierstorfer J. New energetic materials featuring tetrazoles and nitramines–synthesis, characterization and properties. Z Anorg Allg Chem 2010;636(5):735–49.

[43] Thottempudi V, Gao H, Shreeve JM. Trinitromethyl-substituted 5-nitro-or 3-azo-1, 2, 4-triazoles: synthesis, characterization, and energetic properties. J Am Chem Soc 2011;133(16):6464–71.

[44] Naithani N, George BK. Detonation performance of oxygen-rich trinitromethylsubstituted pyrazoles: an in-silico investigation15. Central European Journal of Energetic Materials; 2018.

[45] He C, Shreeve JM. Potassium 4, 5-bis (dinitromethyl) furoxanate: a green primary explosive with a positive oxygen balance. Angew Chem 2016;128(2):782–5.

[46] Zhang Y, Li Y, Hu J, Ge Z, Sun C, Pang S. Energetic C-trinitromethyl-substituted pyrazoles: synthesis and characterization. Dalton Trans 2019;48(4):1524–9.

[47] Dalinger IL, Vatsadze IA, Shkineva TK, Kormanov AV, Struchkova MI, Suponitsky KY, Bragin AA, Monogarov KA, Sinditskii VP, Sheremetev AB. Novel highly energetic pyrazoles: N-Trinitromethyl-Substituted nitropyrazoles. Chem Asian J 2015;10(9):1987–96.

[48] Kettner MA, Klapötke TM. New energetic polynitrotetrazoles. Chem A Eur J 2015;21(9):3755–65.

[49] Haiges R, Christe KO. Energetic high-nitrogen compounds: 5-(trinitromethyl)-2 H-tetrazole and-tetrazolates, preparation, characterization, and conversion into 5-(dinitromethyl) tetrazoles. Inorg Chem 2013;52(12):7249–60.

[50] Yu Q, Imler GH, Parrish DA, Shreeve JM. Challenging the limits of nitro groups associated with a tetrazole ring. Org Lett 2019;21(12):4684–8.

[51] Zhao B, Li X, Wang P, Ding Y, Zhou Z. A novel facile transformation to 1, 2-bis (3-nitro-1-(1 H-tetrazol-5-yl)-1 H-1, 2, 4-triazol-5-yl) hydrazine salts. New J Chem 2018;42(17):14087–90.

[52] Zhang Q, Zhang J, Parrish DA, Shreeve JM. Energetic N-Trinitroethyl-Substituted mono-, di-, and triaminotetrazoles. Chem A Eur J 2013;19(33):11000–6.

[53] Kumar D, He C, Mitchell LA, Parrish DA, Shreeve JM. Connecting energetic nitropyrazole and aminotetrazole moieties with N, N′-ethylene bridges: a promising approach for fine tuning energetic properties. J Mater Chem 2016;4(23):9220–8.

[54] Tang J, Yang P, Yang H, Xiong H, Hu W, Cheng G. A simple and efficient method to synthesize high-nitrogen compounds: incorporation of tetrazole derivatives with N5 chains. Chem Eng J 2020:124027.

[55] Wu J-T, Zhang JG, Yin X, Cheng Z-Y, Xu CX. 3, 4-Diamino-1, 2, 4-triazole based energetic salts: synthesis, characterization, and energetic properties. New J Chem 2015;39(7):5265–71.

[56] Piercey DG, Chavez DE, Scott BL, Imler GH, Parrish DA. An energetic triazolo-1, 2, 4-triazine and its N-oxide. Angew Chem Int Ed 2016;55(49):15315–8.

[57] Kommu N, Balaraju M, Ghule VD, Sahoo AK. Synthetic manifestation of nitro substituted tetrazole-N-(hetero) aryl derivatives and energetic studies. J Mater Chem 2017;5(16):7366–71.

[58] Hervé G, Roussel C, Graindorge H. Selective preparation of 3, 4, 5-trinitro-1H-pyrazole: a stable All-carbon-nitrated arene. Angew Chem Int Ed 2010;49(18):3177–81.

[59] Dalinger IL, Vatsadze IA, Shkineva TK, Popova GP, Shevelev SA. Efficient procedure for high-yield synthesis of 4-substituted 3, 5-dinitropyrazoles using 4-chloro-3, 5-dinitropyrazole. Synthesis 2012;44(13):2058–64.

[60] Izsak D, Klapötke TM, Pflüger C. Energetic derivatives of 5-(5-amino-2 H-1, 2, 3-triazol-4-yl)-1 H-tetrazole. Dalton Trans 2015;44(39):17054–63.

[61] Dalinger IL, Kormanov AV, Suponitsky KY, Muravyev NV, Sheremetev AB. Pyrazole–tetrazole hybrid with trinitromethyl, fluorodinitromethyl, or (difluoroamino) dinitromethyl groups: high-performance energetic materials. Chem Asian J 2018;13(9):1165–72.

[62] Wang Q, Shao Y, Lu M. Amino-tetrazole functionalized fused triazolo-triazine and tetrazolo-triazine energetic materials. Chem Commun 2019;55(43):6062–5.

[63] Temple Jr C, McKee RL, Montgomery JA. Studies on the azidoazomethine-tetrazole equilibrium. II. 4-Azidopyrimidines1. J Org Chem 1965;30(3):829–34.

[64] Tang Y, Huang W, Imler GH, Parrish DA, Shreeve JM. Enforced planar FOX-7-like molecules: a strategy for thermally stable and insensitive π-conjugated energetic materials. J Am Chem Soc 2020;142(15):7153–60.

[65] Tang Y, Ma J, Imler GH, Parrish DA, Shreeve JM. Versatile functionalization of 3, 5-diamino-4-nitropyrazole for promising insensitive energetic compounds. Dalton Trans 2019;48(38):14490–6.

[66] Kumar D, Imler GH, Parrish DA, Shreeve JM. Aminoacetonitrile as precursor for nitrogen rich stable and insensitive asymmetric N-methylene-C linked tetrazole-based energetic compounds. J Mater Chem 2017;5(32):16767–75.

[67] Huang W, Tang Y, Imler GH, Parrish DA, Shreeve JM. Nitrogen-rich tetrazolo [1, 5-b] pyridazine: promising building block for advanced energetic materials. J Am Chem Soc 2020;142(7):3652–7.

[68] Liang L, Wang K, Bian C, Ling L, Zhou Z. 4-Nitro-3-(5-tetrazole) furoxan and its salts: synthesis, characterization, and energetic properties. Chem A Eur J 2013;19(44):14902–10.

[69] Demko ZP, Sharpless KB. Preparation of 5-substituted 1 H-tetrazoles from nitriles in water. J Org Chem 2001;66(24):7945–50.

[70] Dachs M, Dippold AA, Gaar J, Holler M, Klapötke TM. A comparative study on insensitive energetic derivatives of 5-(1, 2, 4-triazol-C-yl)-tetrazoles and their 1-Hydroxy-tetrazole analogues. Z Anorg Allg Chem 2013;639(12-13):2171–80.

[71] Dippold AA, Klapötke TM. Synthesis and characterization of 5-(1, 2, 4-Triazol-3-yl) tetrazoles with various energetic functionalities. Chem Asian J 2013;8(7):1463–71.

[72] Dippold AA, Izsak D, Klapötke TM. A study of 5-(1, 2, 4-triazol-C-yl) tetrazol-1-ols: combining the benefits of different heterocycles for the design of energetic materials. Chem A Eur J 2013;19(36):12042–51.

[73] Tang Y, He C, Imler GH, Parrish DA, Shreeve JM. Design and synthesis of N-methylene-C linked tetrazole and nitramino-1, 2, 4-triazole: an approach to promising energetic materials. J Mater Chem 2016;4(36):13923–9.

[74] Fischer D, Klapötke TM, Stierstorfer J. 1, 5-di (nitramino) tetrazole: high sensitivity and superior explosive performance. Angew Chem Int Ed 2015;54(35):10299–302.

[75] Lin Q-H, Li Y-C, Qi C, Liu W, Wang Y, Pang SP. Nitrogen-rich salts based on 5-hydrazino-1H-tetrazole: a new family of high-density energetic materials. J Mater Chem 2013;1(23):6776–85.

[76] Shreeve JM, Gao H, Wang T. Functionalized tetrazole energetics: a route to enhanced performance. Zeitschrift für anorganische und allgemeine Chemie; 2020.

[77] Dippold AA, Klapötke TM. A study of dinitro-bis-1, 2, 4-triazole-1, 1′-diol and derivatives: design of high-performance insensitive energetic materials by the introduction of N-oxides. J Am Chem Soc 2013;135(26):9931–8.

[78] Tang Y, Yang H, Wu B, Ju X, Lu C, Cheng G. Synthesis and characterization of a stable, catenated N11 energetic salt. Angew Chem Int Ed Engl 2013;52(18):4875–7.

[79] Li Y, Liu W, Pang S. Synthesis and characterization of 5-nitro-2-nitratomethyl-1, 2, 3, 4-tetrazole: a high nitrogen energetic compound with good oxygen

balance. Molecules 2012;17(5):5040–9.
[80] Zhang S, Gao Z, Lan D, Jia Q, Liu N, Zhang J, Kou K. Recent advances in synthesis and properties of nitrated-pyrazoles based energetic compounds. Molecules 2020;25(15):3475.
[81] Zhang J, Parrish DA, Shreeve JM. Thermally stable 3, 6-dinitropyrazolo [4, 3-c] pyrazole-based energetic materials. Chem Asian J 2014;9(10):2953–60.
[82] Xia H, Zhang W, Jin Y, Song S, Wang K, Zhang Q. Synthesis of thermally stable and insensitive energetic materials by incorporating the tetrazole functionality into a fused-ring 3, 6-dinitropyrazolo-[4, 3-c] pyrazole framework. ACS Appl Mater Interfaces 2019;11(49):45914–21.
[83] Kumar D, Imler GH, Parrish DA, Shreeve JM. Aminoacetonitrile as precursor for nitrogen rich stable and insensitive asymmetric N-methylene-C linked tetrazole-based energetic compounds. J Mater Chem 2017;5(32):16767–75.
[84] Joo Y-H, Shreeve JM. Nitroimino-tetrazolates and oxy-nitroimino-tetrazolates. J Am Chem Soc 2010;132(42):15081–90.
[85] Joo YH, Shreeve JM. High-density energetic mono-or bis (oxy)-5-nitroiminotetrazoles. Angew Chem Int Ed 2010;49(40):7320–3.
[86] Kumar D, Mitchell LA, Parrish DA, Shreeve JM. Asymmetric N, N′-ethylene-bridged azole-based compounds: two way control of the energetic properties of compounds. J Mater Chem 2016;4(25):9931–40.
[87] Dippold AA, Izsák D, Klapötke TM, Pflüger C. Combining the advantages of tetrazoles and 1, 2, 3-triazoles: 4, 5-bis (tetrazol-5-yl)-1, 2, 3-triazole, 4, 5-bis (1-hydroxytetrazol-5-yl)-1, 2, 3-triazole, and their energetic derivatives. Chem A Eur J 2016;22(5):1768–78.