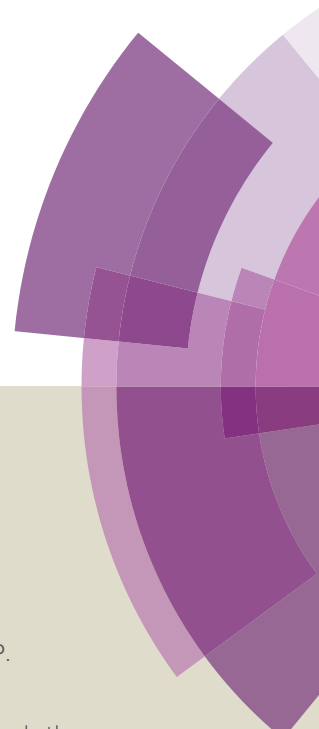


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Polynitro-substituted Pyrazoles and Triazoles as Potential Energetic Materials and Oxidizers

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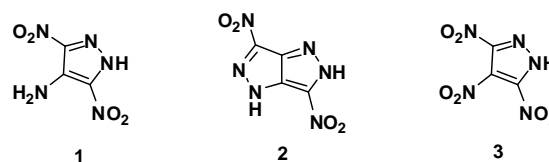
N-Trinitroethylamino energetic derivatives were obtained from carbon and nitrogen functionalization of nitropyrazoles and nitrotriazoles. *N*-Trinitroethylamino nitroazoles and *N*-amino nitroazoles were fully characterized by IR, multinuclear NMR spectra, and elemental analyses. Compounds **10**, **11** and **15** were further confirmed by single crystal X-ray structuring. *N*-Functionalized nitroazoles have moderate to excellent thermal stabilities with good densities. Data based on impact and friction tests show these compounds range from very sensitive to insensitive. Theoretical calculations carried out using Gaussian 03 demonstrate good to excellent detonation pressures and velocities, as well as high specific impulse.

Introduction

Polynitro-functionalized heterocycles are frequently found in high performance energetic materials. Given this background, rational introduction of nitro groups plays a significant role in the design and synthesis of these important compounds. Thus this has become an intense research area in the development of such materials with not only excellent detonation properties, high densities, and positive oxygen balances, but also good thermal stabilities and insensitivities to impact and friction.¹ With an increasing number of nitro groups via *C*- and *N*-functionalization, the densities and performance of molecules are improved, while concomitantly they often can be handled safely only with some difficulty during industrial production and storage. For example, some known high performance explosives such as RDX and HMX, are sensitive to impact and shock.² Therefore, design of polynitro-functionalized compounds is one of the most attractive challenges in the pursuit of ideal energetic materials.

Functionalized polynitropyrazoles, a new family of energetic materials, are competitive candidates for the next generation of advanced energetic materials. The three catenated carbon atoms in pyrazole not only enhance thermal stability and impact insensitivity, but also endow the backbone with an opportunity for a variety of functionalizations, e. g., many *C*-functionalized pyrazoles serve as precursors for construction of fused heterocycles.³ Hence, with increased demand for rational design of energetic materials, functionalization of pyrazole with energetic substituted groups has made progress in the past decade.⁴ For example, 4-amino-3,5-dinitropyrazole (LLM-116, **1**) which was synthesized by amination of 3,5-dinitropyrazole using 1,1,1-trimethylhydrazinium iodide (TMI), exhibits a high density with excellent impact insensitivity.⁵ Studies indicate that highly-dense 3,6-dinitro-1,5-dihydropyrazolo[4,3-*c*]pyrazole (DNPP, **2**) is thermally stable due to its symmetrically fused scaffold.⁶ Additionally, fully *C*-nitrated pyrazoles have been

comprehensively studied giving 3,4,5-trinitropyrazole (TNP, **3**) as a promising energetic material (Scheme 1).⁷



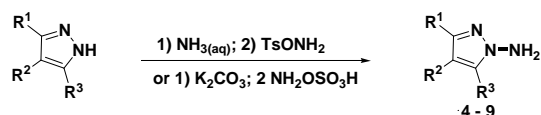
Scheme 1. Examples of pyrazole-based energetic materials.

Functionalization at carbon provides a large number of pyrazole-based energetic materials with high performance characteristics, whereas less attention has been devoted to nitrogen-functionalization. For example, both *C*- and *N*-nitrated pyrazoles have been examined to give 1,3,4-trinitropyrazole, which is very moisture sensitive.⁸ Compared with *N*-nitration of azoles, *N*-trinitroethylamination is considered to be a more favorable strategy giving rise to remarkable improvements in densities and detonation properties.⁹ More importantly, they are stable enough to be handled safely. In spite of wide application to acyclic energetic molecules,¹⁰ trinitroethylamino groups bonded to nitrogen-rich heterocycles, especially to nitro-substituted azoles, are rather rare.¹¹ Due to the low activity, *N*-trinitroethylamination of fully substituted nitroazoles remains a difficult challenge. In our continuing efforts to prepare new high performance polynitro compounds, we now report our attempts to design and synthesize a new class of fully substituted nitropyrazoles using a *N*-trinitroethylamino functionalized strategy. For comparison, some *N*-trinitroethylamino nitrotriazoles have been synthesized also. All of the *N*-trinitroethylamino nitropyrazoles and nitrotriazoles have been fully characterized, and, in some cases, their structures have been further verified by single crystal X-ray diffraction.

Results and Discussion

Synthesis

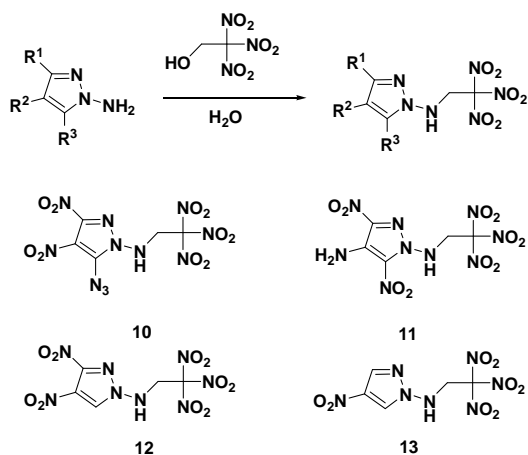
Various C-functionalized nitropyrazoles have been synthesized by known methods.¹² *N*-Amination of polynitropyrazoles, however, has not been fully explored since only a few *N*-amino nitropyrazoles have been reported and they were not fully characterized.¹³ Thus, it was useful to develop a general method to aminate a variety of nitropyrazoles. In an initial study, amination of pyrazoles using *O*-tosylhydroxylamine with ammonium nitropyzolates led readily to *N*-amino nitropyrazoles in moderate to good yields for most nitropyrazoles (5–9). Although amination of 4-nitropyrazole with *O*-tosylhydroxylamine only produced trace amounts of 1-amino-4-nitropyrazole (4), its reaction with hydroxylamine-*O*-sulfonic acid and potassium carbonate gave the desired product in 75% yield (Scheme 2).



4 $R^1 = R^3 = \text{H}, R^2 = \text{NO}_2$; 5 $R^1 = R^3 = \text{NO}_2, R^2 = \text{H}$; 6 $R^1 = R^2 = \text{NO}_2, R^3 = \text{H}$
7 $R^1 = R^2 = \text{NO}_2, R^3 = \text{CN}$; 8 $R^1 = R^2 = \text{NO}_2, R^3 = \text{N}_3$; 9 $R^1 = R^3 = \text{NO}_2, R^2 = \text{NH}_2$

Scheme 2 Amination of nitropyrazoles.

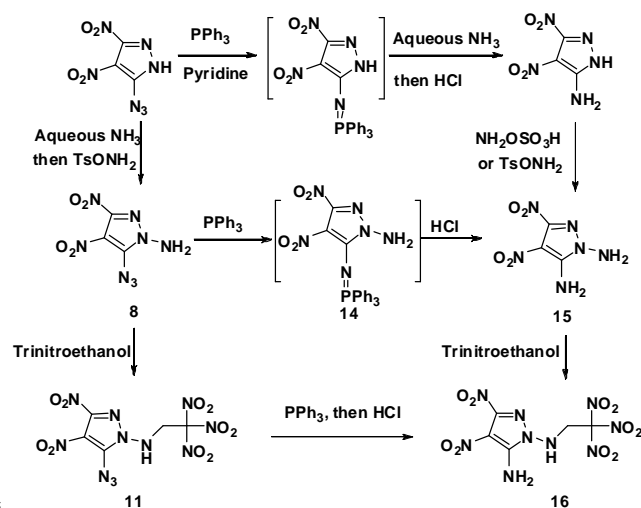
After prefunctionalization with the amino group, further *N*-trinitroethylation reactions were continued in order to obtain more energetic pyrazoles. Owing to the electron-withdrawing effect of substituent groups bonded to the pyrazole ring, some *N*-amino nitropyrazoles, such as 1-amino-3,5-dinitropyrazole (5) and 1-amino-3,4-dinitro-5-cyanopyrazole (7), failed to undergo Mannich reactions with trinitroethanol. Fully substituted nitropyrazoles including 1-amino-3,4-dinitro-5-azidopyrazole (8) and 1,4-diamino-3,5-dinitropyrazole (9) reacted readily with trinitroethanol to produce the corresponding *N*-trinitroethylamino pyrazoles (10 and 11). Additionally, trinitroethylation of 4 and of 1-amino-3,4-dinitro pyrazole (6) gave 12 and 13 as well (Scheme 3).



Scheme 3 Syntheses of *N*-trinitroethylamino pyrazoles.

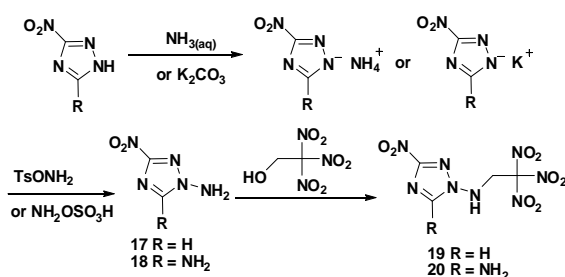
In our previous studies, 1,4-diamino-3,5-dinitropyrazole was shown to exhibit excellent density and detonation properties due to the strong hydrogen bonds between neighboring NH_2 and NO_2 groups.^{4d} For comparison, it was of interest to examine the analogous properties of its isomer, 1,5-diamino 3,4-dinitropyrazole. However, attempted amination of this

compound using hydroxylamine-*O*-sulfonic acid or *O*-tosylhydroxylamine failed to yield the corresponding *N*-amino product. Therefore, an alternative synthetic strategy was employed which involved amination of 3,4-dinitro-5-azidopyrazole, followed by reduction and hydrolysis to yield 1,5-diamino 3,4-dinitropyrazole (15). Additionally, *N*-trinitroethylamino-5-diamino 3,4-dinitropyrazole was prepared readily by condensation of 1,5-diamino 3,4-dinitropyrazole and trinitroethanol in aqueous solution. However, attempts to prepare 16 by reducing 5-azido-3,4-dinitro-*N*-(2,2,2-trinitroethyl)-1H-pyrazol-1-amine (11) failed (Scheme 4).



Scheme 4 Syntheses of 1,5-diamino-3,4-dinitropyrazole and its trinitroethylamino derivatives.

N-Trinitroethylamino 1,2,4-triazoles were examined as different azole-based analogues for comparison of reaction activity and properties. Trinitroethylation of fully *C*-nitrated 3,5-dinitro-1H-1,2,4-triazol-1-amine failed; however, 3-nitro-1H-1,2,4-triazol-1-amine (17), which was obtained from 3-nitro-1H-1,2,4-triazole, could be trinitroethylated smoothly in trinitroethanol (Scheme 5). Likewise, when treated with K_2CO_3 and hydroxylamine-*O*-sulfonic acid, 3-nitro-1H-1,2,4-triazole-1,5-diamine (18) formed by *N*-amination of 3-nitro-1H-1,2,4-triazol-5-amine. Subsequently, trinitroethylation of 17 and 18 provide the corresponding *N*-trinitroethylamino triazoles 19 and 20, respectively.



Scheme 5 Syntheses of *N*-trinitroethylamino nitrotriazoles.

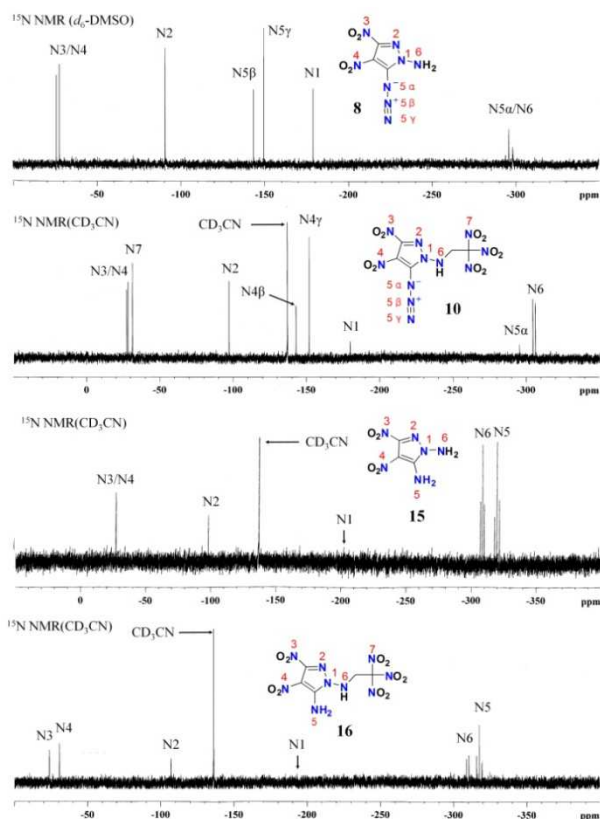


Figure 1 Selected ^{15}N NMR spectra of *N*-amino pyrazoles and corresponding *N*-trinitroethylamino pyrazoles.

NMR Spectroscopy

These new energetic materials were confirmed by IR, and ^1H and ^{13}C NMR spectra, and elemental analyses. Characteristic absorption bands of NH_2 and NH groups were observed for both *N*-amino and *N*-trinitroethylamino pyrazoles at $3000\text{--}3400\text{ cm}^{-1}$ in the infrared spectra. Also, strong absorption bands assignable to the nitro groups were observed at $1300\text{--}1600\text{ cm}^{-1}$. In the ^1H NMR spectra, signals of NH_2 and NH were found at $5.5\text{--}7.5\text{ ppm}$ in CD_3CN as the solvent. The chemical shifts of the carbon atoms bonded directly to three nitro groups in the ^{13}C NMR spectra of **10**, **12** and **16** are at $\sim 127.7\text{ ppm}$, which is in general agreement with the literature.^{11c} Due to poor solubility, the ^{13}C NMR spectra for **11**, **19**, and **20** could not be recorded.

In addition to ^1H and ^{13}C NMR spectra, the ^{15}N NMR spectra aid in characterization, especially for nitrogen-rich compounds. As is shown in Figure 1, the selected *N*-amino pyrazoles (**8** and **15**) and their corresponding *N*-trinitroethylamino pyrazoles (**10** and **16**) are displayed as measured in CD_3CN with the exception of **8**, which was measured in $d_6\text{-DMSO}$. The ^{15}N signals of the nitro group bonded to a pyrazole ring can be assigned to resonances ranging from $\delta = -23$ to -28 ppm , whereas the signals of trinitroethyl group appeared at about $\delta = -30\text{ ppm}$. For **10**, the three signals for azide were found at $\delta = -142.34$ ($\text{N}\beta$), -151.40 ($\text{N}\alpha$), and -294.98 ($\text{N}\gamma$) ppm. In the spectra of **15** and **16**, signals at highest field are attributed to amino groups. For identification with ^1H and ^{15}N -HMBC spectra (See Supporting Information), NH and NH_2 groups of **15** are assigned to $\delta = -308.27$ and -319.44 ppm , respectively. The resonances of **16** agree well at $\delta = -309.50$ (NH) and -317.48 (NH_2). Although signals of N1 are

weak, the ^1H and ^{15}N -HMBC spectra show strong nitrogen-proton coupling, originating from neighboring amino groups (See Supporting Information).

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Physical and Computational Properties

Thermal stabilities of these compounds were determined by differential scanning calorimetric (DSC) measurements (Table 1). With the exception of **18**, all of the *N*-amino compounds have melting points ranging from $58\text{ }^\circ\text{C}$ to $139\text{ }^\circ\text{C}$. Although the azido-functionalized pyrazole (**8**) decomposes at $120\text{ }^\circ\text{C}$, the remaining *N*-amino pyrazoles and triazoles have relatively high decomposition temperatures ($195\text{ }^\circ\text{C} - 306\text{ }^\circ\text{C}$). The *N*-trinitroethylamino compounds decompose without melting at moderate temperatures ($108\text{ }^\circ\text{C} - 141\text{ }^\circ\text{C}$). Densities of these energetic compounds which are in the range of 1.57 g cm^{-3} to 1.83 g cm^{-3} were determined using a gas pycnometer. Among them, six compounds, **8**, **10**, **11**, **15**, **16**, and **20**, show a higher density than RDX (1.80 g cm^{-3}). It is found that the introduction of an amino group enhances density, e.g., for **6** (1.71 g cm^{-3}), **15** (1.82 g cm^{-3}), **12** (1.78 g cm^{-3}), and **16** (1.83 g cm^{-3}).

Oxygen balance (OB) is a significant index of energetic materials, which indicates the deficiency or excess of oxygen in a compound required to convert all carbon into carbon monoxide and all hydrogen into water. *N*-Amino pyrazoles and triazoles exhibit negative oxygen balance ranging from -37.5 to 0% , while *N*-trinitroethylamino functionalized pyrazoles and triazoles have positive OB values ranging from 2.8 to 14.9% , arising mainly from the introduction of trinitroethyl groups.

As shown in Table 1, the heats of formation of *N*-amino nitropyrazoles and *N*-amino nitrotriazoles are in the range of 0.92 kJ g^{-1} to 2.56 kJ g^{-1} , whereas the heats of formation of *N*-trinitroethylamino compounds fall between 0.32 kJ g^{-1} to 1.30 kJ g^{-1} . With these data in hand, the detonation pressures (P), velocities (v_D), and specific impulses (I_{sp}) were calculated by using EXPLO 6.01. All *N*-amino nitropyrazoles and nitrotriazoles exhibit good or excellent detonation pressures ($20.1\text{ GPa} - 35.8\text{ GPa}$) and detonation velocities ($7464\text{ m s}^{-1} - 9053\text{ m s}^{-1}$), which in some cases are comparable to triaminotrinitrobenzene (TATB, P 31.7 GPa , v_D 8504 m s^{-1}) or hexogen (RDX, P 34.9 GPa , v_D 8795 m s^{-1}). Owing to azido-functionalization, compounds **8** and **10** have the highest heats of formation, as well as the best detonation performances (**8**, P , 35.8 GPa ; v_D , 9053 m s^{-1} ; **10**, P , 35.6 GPa ; v_D , 8968 m s^{-1}). However, they are impact and friction sensitive (**8**, IS , 1.5 J , FS , 5 N ; **10**, 2.5 J , FS , 20 N). Amino-substituted compounds are less sensitive but exhibit similar detonation performance, e. g., **11** (P , 34.3 GPa ; v_D , 8745 m s^{-1} , IS , 12 J , FS , 120 N) and **16** (P , 35.0 GPa ; v_D , 8803 m s^{-1} , IS , 8 J , FS , 80 N). Additionally, the detonation performance of insensitive compound **15** (P , 32.8 GPa ; v_D , 8689 m s^{-1} , IS , $>40\text{ J}$, FS , 360 N) is superior to the traditional energetic compound TATB (P , 31.7 GPa ; v_D , 8504 m s^{-1} , IS , 50 J , FS , 360 N), and approaches RDX (P , 34.9 GPa ; v_D , 8795 m s^{-1} , IS , 7 J , FS , 120 N).

Table 1 Properties of the *N*-functionalized energetic compounds.

Compd	T_m^a [°C]	T_d^b [°C]	d^c [g cm ⁻³]	$\Delta H_f(g)^d$ [kJ mol ⁻¹]	ΔH_{sub}^e [kJ mol ⁻¹]	ΔH_f^f [kJ mol ⁻¹]/[kJ g ⁻¹]	P^g [GPa]	v_D^h [m s ⁻¹]	IS^i [J]	FS^j [N]	OB^k [%]
4	83	195	1.57	231.1	70.0	164.1/1.28	20.1	7464	>40	360	-37.50
5	113	225	1.76	243.8	72.6	171.2/0.99	30.7	8434	>40	360	-4.62
6	58	241	1.71	262.6	62.3	200.3/1.16	29.3	8309	>40	360	-4.62
7	104	217	1.77	404.7	70.9	333.8/1.69	29.6	8379	>40	360	-8.08
8	120	121	1.82	622.1	73.9	548.2/2.56	35.8	9053	1.5	5	0
10	-	117	1.82	565.6	73.9	491.7/1.30	35.6	8968	2.5	20	14.85
11	-	116	1.81	199.5	75.4	124.1/0.35	34.3	8745	12	120	11.40
12	87	110	1.78	210.0	67.7	142.3/0.42	33.1	8667	6	80	14.29
13	109	112	1.74	212.7	71.8	140.9/0.48	30.8	8390	15	360	2.75
15	133	254	1.82	249.4	76.4	173.0/0.92	32.8	8689	>40	360	-8.51
16	-	106	1.83	184.6	72.6	112.0/0.32	35.0	8803	8	80	11.40
17	139	306	1.68	279.2	77.5	201.7/1.56	25.9	8174	>40	360	-18.60
18	-	244	1.76	247.6	103.1	144.5/1.00	27.4	8440	>40	360	-22.22
19	-	141	1.79	240.3	79.7	160.6/0.55	33.5	8711	6	60	10.95
20	-	108	1.82	201.8	76.7	125.1/0.41	34.7	8828	7	60	7.82
TNT	81	295	1.65	-	-	-295/-1.38	19.5	6881	15	-	-24.67
TATB	324	324	1.93	-	-	-140/-0.54	31.7	8504	50	360	-18.60
RDX	205	230	1.80	-	-	85/0.42	34.9	8795	7	120	0.00

^a Melting temperature. ^b Decomposition temperature (onset). ^c Density measured by gas pycnometer (25 °C). ^d Gas phase enthalpy of formation. ^e Enthalpy of sublimation (calculated with Trouton's rule). ^f Heat of formation. ^g Detonation pressure (calculated with Explot 6.01). ^h Detonation velocity (calculated with Explot 6.01). ⁱ Impact sensitivity. ^j Friction sensitivity. ^k Oxygen balance (based on CO) for C_aH_bO_cN_d, 1600(c-a-b/2)/MW, MW = molecular weight.

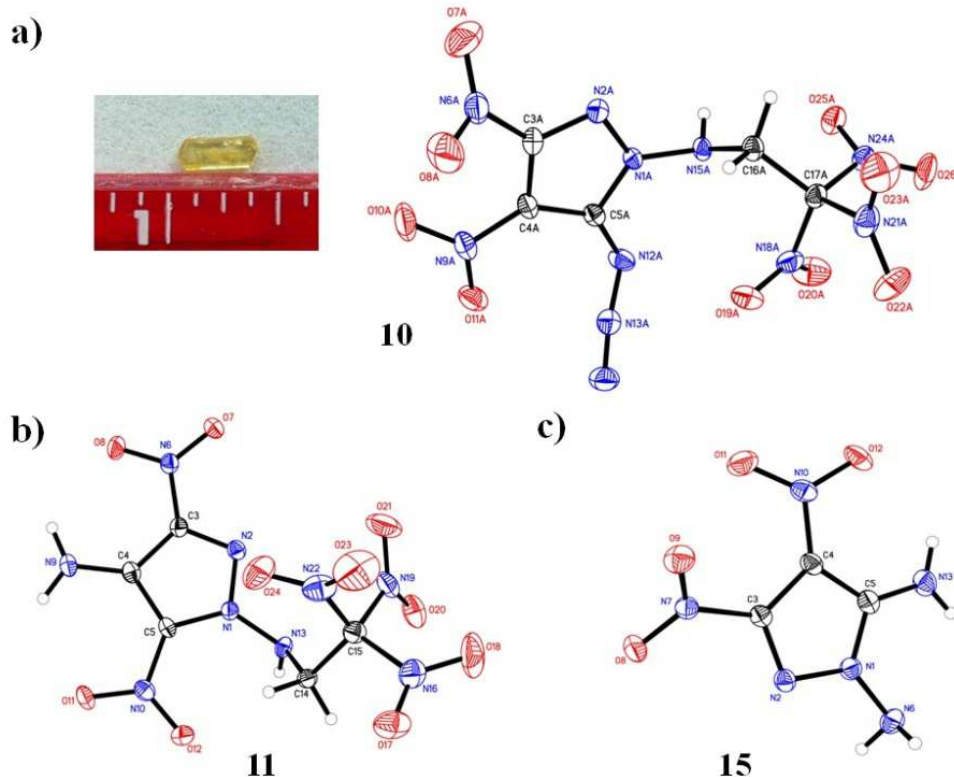


Figure 2 (a). Single-crystal X-ray structure of **10**. The scale is in inches (b). Single-crystal X-ray structure of **11**. (c). Single-crystal X-ray structure of **15**.

Table 2 Crystallographic data for **10**, **11**, and **15**.

Compound	10	11	15
Empirical formula	C ₅ H ₅ N ₉ O ₁₀	C ₅ H ₃ N ₁₁ O ₁₀	C ₃ H ₄ N ₆ O ₄
Formula weight	351.18	377.18	188.12
CCDC number	927840	948453	948454
Crystal size [mm ³]	0.48 x 0.34 x 0.06	0.25 x 0.24 x 0.02	0.56 x 0.52 x 0.39
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	Pbca	P2 ₁ /c	Pbca
a [Å]	11.0318(17)	18.9685(7)	12.7023(12)
b [Å]	10.0035(15)	7.7374(3)	8.0688(8)
c [Å]	22.999(3)	27.7321(10)	13.0694(12)
α [°]	90	90	90
β [°]	90	91.248(1)	90
γ [°]	90	90	90
V [Å ³]	2538.1(7)	4069.2(3)	1339.5(2)
Z	8	12	8
T[K]	150(2)	150(2)	150(2)
ρ _{calcd} [Mg m ⁻³]	1.838	1.847	1.866
μ[mm ⁻¹]	0.177	0.177	0.170
F(000)	1424	2280	768
θ [°]	1.77 to 26.50	1.07 to 26.39	3.12 to 26.45
Index ranges	-13<=h<=13, -10<=k<=12, -28<=l<=28	-23<=h<=23, -9<=k<=5, -34<=l<=33	-15<=h<=15, -9<=k<=10, -16<=l<=16
Reflections collected	21706	24435	11756
Independent reflections (R _{int})	2606 [R _{int} = 0.0504]	8235 [R _{int} = 0.0331]	1379 [R _{int} = 0.0251]
Data/restraints/parameters	2606 / 0 / 220	2270 / 1 / 208	1379 / 0 / 131
Goodness-of-fit on F ²	1.045	1.017	1.072
R ₁ (I > 2σ(I)) ^a	0.0351	0.0373	0.0265
wR ₂ (I > 2σ(I)) ^b	0.0840	0.0822	0.0689
R ₁ (all data)	0.0441	0.0599	0.0280
wR ₂ (all data)	0.0882	0.0919	0.0703
Largest diff. peak and hole ([e Å ⁻³])	0.315 and -0.235	0.271 and -0.265	0.370 and -0.173

$$^a R_1 = \sum ||F_o| - |F_c| || / \sum |F_o|; \quad ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

X-Ray Crystallography

Crystals of **10**, **11** and **15** were mounted on a MiteGen MicroMesh using a small amount of Cargille Immersion Oil. Compounds **10** and **11** suitable for crystal-structure analysis were obtained by recrystallization from hexane and acetone, whereas **15** was recrystallized from hexane and acetonitrile. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated MoK_α radiation (λ = 0.71073). An Oxford Cobra low temperature device was used to keep the crystals at a constant 150(2) K during data collection. Data collection was performed and the unit cell was initially refined using APEX2 [v2010.3-0].¹⁴ Data reduction was performed using SAINT [v7.68A]¹⁵ and XPREP [v2008/2].¹⁶ Corrections were applied for Lorentz, polarization, and absorption effects using SADABS [v2008/1].¹⁷ The structure was solved and refined with the aid of the programs in the SHELXTL-plus [v2008/4] system of programs.¹⁸ The full-matrix least-squares refinement on F² included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model. Crystallographic data and structures are shown in Figure 2 and Table 2, respectively. Compounds **10** and **11** crystallize in the orthorhombic Pbca space group, whereas **15** crystallizes in the monoclinic P2₁/c space group. The calculated densities at 150 K are 1.847 g cm⁻³ for **10**, 1.838 g cm⁻³ for **11**, and 1.866 g cm⁻³ for **15**. For **11**, the lengths of

C–N bonds (1.514(2) Å, 1.529(2) Å; C(15)–N(19), 1.514(2) Å; C(15)–N(16), 1.522(2) Å; C(15)–N(22), 1.529(2) Å) in trinitroethyl groups are longer than the others C–N bonds of C–NO₂ (C(3)–N(6), 1.420(2), C(5)–N(10), 1.3986(19)). Based on the torsion angles (N(6)–C(3)–C(4)–C(5), 179.09(14), N(1)–N(2)–C(3)–N(6), 178.57(13), N(13)–N(1)–N(2)–C(3), 177.49(12), C(4)–C(3)–N(6)–O(7), 170.43(14), N(2)–C(3)–C(4)–N(9), 179.91(15), N(1)–C(5)–N(10)–O(11), -175.30(14)), nitro and amino groups bonded to pyrazole are nearly planar with the backbone. However, for **10** and **15**, nitro groups bonded to the pyrazole ring are considerably twisted relative to each other with various torsion angles (e.g., **10**, C(4A)–C(3A)–N(6A)–O(7A), -138.2(2), C(4C)–C(3C)–N(6C)–O(7C), 50.6(3); **15**, C(4)–C(3)–N(7)–O(9), -39.84(16), N(2)–C(3)–N(7)–O(8), -43.33(13)). Intermolecular hydrogen bonds between amino groups and nitro groups are found in all crystals, such as **10** (N(13)–H(13)...O(8)#3), **11** (N(15A)–H(15A)...O(10C)#1), and **15** (N(6)–H(6A)...O(11)#1).

Conclusions

A family of N-functionalized compounds has been synthesized in moderate to excellent yields by amination and trinitroethylation reactions of nitropyrazoles and nitrotriazoles. All compounds are fully characterized by analytical and spectroscopic methods. Furthermore, **10**, **11**, and **15** were structured using single-crystal X-ray diffraction. Full functionalization of pyrazoles and triazoles, including C-substitution and N-substitution, causes these nitrogen-rich backbones to have remarkably good detonation

performances. For example, **8** and **10** have excellent detonation pressures and velocities but with high sensitivity to impact and friction. In contrast, **11** is less sensitive and has a favorable detonation performance (P , 34.3 GPa; v_D , 8745 m s⁻¹, IS, 12 J, FS, 120 N), which is comparable RDX. Some *N*-amino compounds also exhibit good thermal stabilities and detonation performances (e. g., **15**, P , 32.8 GPa; v_D , 8689 m s⁻¹, IS, >40 J, FS, 360 N). Additionally, several *N*-trinitroethylamino derivatives (**10**, **11**, **12**, **15**, and **19**) with an oxygen balance over 10% are potential energetic oxidizers for propellant ingredients.

Experimental section

Safety precautions

Although we have not encountered any difficulties in preparing these compounds, manipulations must be carried out by using appropriate standard safety precautions. Eye protection and leather gloves must be worn. Mechanical actions of these energetic materials involving scratching or scraping particularly with metal spatulas must be avoided.

General Methods

¹H and ¹³C NMR spectra were recorded on a Bruker 300 MHz nuclear magnetic resonance spectrometer operating at 300 MHz and 75 MHz, respectively. ¹⁵N NMR spectra were recorded on a Bruker 500 MHz nuclear magnetic resonance spectrometer operating at 50.7 MHz. Chemical shifts for ¹H, and ¹³C NMR spectra are reported relative to (CH₃)₄Si and for ¹⁵N NMR to CH₃NO₂. CD₃CN was used as a locking solvent unless otherwise stated. Elemental analyses (C, H, N) were performed on a CE-440 Elemental Analyzer. Melting and decomposition (onset) points were recorded on a differential scanning calorimeter (DSC, TA Instruments Q10) at a scan rate of 5 °C min⁻¹. Impact and friction sensitivity measurements were made using a standard BAM Fallhammer and a BAM friction tester. IR spectra were recorded using KBr pellets with a Biorad Model 3000 FTS spectrometer. Densities were determined at room temperature by employing a Micromeritics AccuPyc 1330 gas pycnometer.

Theoretical study

Computations were performed by using the Gaussian 03 (Revision D.01) suite of programs.¹⁹ The geometric optimization of the structures and frequency analyses were carried out by using the B3-LYP functional with the 6-31+G** basis set, and single-point energies were calculated at the MP2/6-311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. The gas phase enthalpies of formation were computed and the enthalpy of reaction is obtained by combining the MP2/6-311++G** energy difference for the reactions, the scaled zero point energies, and other thermal factors. Thus, the gas phase enthalpy of the species being investigated can be readily extracted. The enthalpy of sublimation was calculated by using Trouton's rule.²⁰ Solid-state heats of formation of the resulting compounds were calculated with Equation (1) in which T_m is the melting temperature.

$$\Delta H_f = \Delta H_f(g) - \Delta H_{sub} = \Delta H_f(g) - 188[\text{J mol}^{-1} \text{K}^{-1}] \times T_m \quad (1)$$

Detonation pressure (P) and velocity (v_D) were calculated using the program package EXPLO 6.01.

O-Tosylhydroxylamine: Freshly prepared ethyl *O*-*p*-tolylsulfonylethoxyacetohydroximate (15 mmol, 3.86 g) was added to 25 mL of 60% HClO₄. The mixture was stirred at room temperature for 2 h. Hydrolysis of ethyl *O*-*p*-tolylsulfonylethoxyacetohydroximate was monitored by thin layer chromatography (TLC). When the reaction was complete, the white slurry was poured into ice and extracted with CH₂Cl₂ (4×25 mL). The organic portions were combined, dried over Na₂SO₄, and used for *N*-amination reactions. All nitropyrazoles and nitrotriazoles were synthesized according to the literature.^{10,21}

4-Nitro-1*H*-pyrazol-1-amine (4): A mixture of 4-nitropyrazole (339 mg, 3 mmol, 1 equiv), K₂CO₃ (4.15 g, 30 mmol, 10 equiv) and distilled water (20 mL) was stirred at 60 °C until a clear solution was obtained. To the reaction, hydroxylamine-*O*-sulfonic acid (1.02 g, 9 mmol) was added over ten minutes, and the mixture was stirred overnight at 60 °C. The final aqueous solution was extracted by ethyl ether (3×20 mL), and then the combined organic phases were dried over Na₂SO₄. The solvent was removed at reduced pressure to give pure aminated product **4**. White solid (288 mg, 75%). T_m 83 °C, T_{dec} 195 °C; ¹H NMR: δ 8.23 (s, 1H), 7.94 (s, 1H), 5.89 (s, 2H); ¹³C NMR: δ 134.9, 134.2, 129.7; IR (KBr pellet): ν 3352, 3294, 3112, 1630, 1526, 1474, 1406, 1309, 1219, 11184, 978, 955, 905, 816, 756 cm⁻¹; elemental analysis (%) calcd for C₃H₄N₄O₂ (128.09): C, 28.13; H, 3.15; N, 43.74; found: C, 28.16; H, 3.17; N, 43.42.

General procedure for synthesis of *N*-NH₂ pyrazoles (5–9): To a 200 mL round-bottomed flask, a pyrazole (10 mmol) was added to aqueous ammonia (10 mL) and stirred at room temperature for 0.5 h. Then the water was removed by blowing air over the liquid surface and the residue was dried in vacuo. Acetonitrile (100 mL) was added to the ammonium salt, followed by freshly prepared *O*-tosylhydroxylamine in CH₂Cl₂ (100 mL, prepared as above). The mixture was stirred at room temperature for 2 days. NaHCO₃ (0.3g) was added and the final mixture was stirred for additional 0.5h. The solvent was removed by rotary evaporation and ethyl acetate (50 mL) was added. The white precipitate was filtered and ethyl acetate was removed to afford the crude product, which could be further purified by column chromatography.

3,5-Dinitro-1*H*-pyrazol-1-amine (5): Isolated by chromatography with hexane/ethyl acetate (100/20). White solid (1.01 g, 58%). T_m 113 °C, onset T_{dec} 225 °C; ¹H NMR: δ 7.65 (s, 1H), 6.79 (s, 2H); ¹³C NMR: δ 149.3, 143.2, 102.1; IR (KBr pellet): ν 3356, 3289, 3154, 1560, 1508, 1352, 11130, 1093, 1011, 926, 846, 734 cm⁻¹; elemental analysis (%) calcd for C₃H₃N₅O₄ (173.09): C, 20.82; H, 1.75; N, 40.46; found: C, 21.22; H, 1.82; N, 39.80.

3,4-Dinitro-1*H*-pyrazol-1-amine (6): Isolated by chromatography with hexane/ethyl acetate (100/35). Pale yellow solid (1.10 g, 64%). T_m 58 °C, onset T_{dec} 291 °C; ¹H NMR: δ 8.34 (s, 1H), 6.12 (s, 2H); ¹³C NMR: δ 145.5, 132.8, 126.3; ¹⁵N NMR: δ -26.33, -26.39, -77.65, -168.42, -291.57 (t, J = 73.00 Hz); IR (KBr pellet): ν 3142, 1590, 1535, 1510, 1381, 1119, 808 cm⁻¹; elemental analysis (%) calcd for C₃H₃N₅O₄ (173.09): C, 20.82; H, 1.75; N, 40.46; found: C, 21.13; H, 1.69; N, 40.21.

1-Amino-3,4-dinitro-1*H*-pyrazole-5-carbonitrile (7): Isolated by chromatography with hexane/ethyl acetate (100/30). Yellow

solid (1.66 g, 84%). T_m 104 °C, onset T_{dec} 249 °C; 1H NMR: δ 6.41 (s, 2H); ^{13}C NMR: δ 145.2, 129.3, 118.1, 107.1; ^{15}N NMR: δ -30.32, -31.93, -70.33, -96.68, -290.67 (t, $J = 74.53$ Hz); IR (KBr pellet): ν 3331, 3281, 2261, 1629, 1562, 1523, 1364, 1333, 1087, 997, 820, 789 cm^{-1} ; elemental analysis (%) calcd for $C_4H_2N_6O_4$ (198.10): C, 24.25; H, 1.02; N, 42.42; found: C, 23.81; H, 1.08; N, 42.46.

5-Azido-3,4-dinitro-1H-pyrazol-1-amine (8): Isolated by chromatography with hexane/ethyl acetate (100/50). Yellow solid (0.97 g, 45%). T_m 120 °C, onset T_{dec} 133 °C; 1H NMR: δ 5.77 (s, 2H); ^{13}C NMR (d_6 -DMSO): δ 143.8, 136.2, 114.8; ^{15}N NMR (d_6 -DMSO): δ -25.94, -27.72, -90.76, -143.69, -149.85, -179.20, -296.05, -298.41; IR (KBr pellet): ν 3367, 3289, 3240, 2150, 1645, 1560, 1493, 1377, 1338, 1292, 1182, 1128, 1076, 978, 847, 794, 760 cm^{-1} ; elemental analysis (%) calcd for $C_3H_2N_8O_4$ (214.10): C, 16.83; H, 0.94; N, 52.34; found: C, 16.84; H, 0.87; N, 49.87. **Caution!** During elemental analysis the compound exploded and the results could not be obtained when 2.0 mg of sample was used. To prevent a violent explosion, less than 0.5 mg of sample was used which resulted in a large relative error in the nitrogen value.

General procedure for synthesis of N-trinitroethylamino pyrazoles (10–13, 16, 19, and 20): N - NH_2 -pyrazoles (1 mmol) were added to distilled water (for **4**, 30 mL; for **6**, 30 mL; for **8**, 80 mL; for **9**, 150 mL) and were stirred at 80 °C until a clear solution was obtained. The mixture was allowed to cool to 50 °C followed by the addition of 2,2,2-trinitroethanol (362 mg, 2 mmol). The reaction was held at 50 °C for 1h and then stirred overnight at ambient temperature. The precipitate was filtered, washed with water, and dried under vacuum.

5-Azido-3,4-dinitro-N-(2,2,2-trinitroethyl)-1H-pyrazol-1-amine (10): White solid (267 mg, 71%). T_m 117 °C, onset T_{dec} 120 °C; 1H NMR: δ 6.81 (s, 2H); 4.96 (s, 2H); ^{13}C NMR: δ 146.8, 139.7, 127.7, 117.4, 53.0; ^{15}N NMR: δ -26.86, -27.81, -30.82 (t, $J = 2.03$ Hz), -96.71, -142.34, -151.40, -179.49 (t, $J = 3.04$ Hz), -294.98, -304.97 (d, $J = 86.19$ Hz); IR (KBr pellet): ν 3314, 3007, 2170, 1609, 1561, 1505, 1454, 1382, 1341, 1304, 838, 806, 761 cm^{-1} ; elemental analysis (%) calcd for $C_5H_3N_{11}O_{10}$ (377.15): C, 15.92; H, 0.80; N, 40.85; found: C, 16.18; H, 0.58; N, 39.32. To prevent violent explosion, less than 0.5 mg of sample was used which caused a large relative error in the nitrogen value. The structure of **10** is supported by single crystal X-ray analysis.

3,5-Dinitro- N^1 -(2,2,2-trinitroethyl)-1H-pyrazole-1,4-diamine (11): Yellow solid (183 mg, 52%). Onset T_{dec} 128 °C; 1H NMR: δ 7.48 (s, 1H); 6.62 (s, 2H), 4.98 (s, 2H); IR (KBr pellet): ν 3463, 3339, 1630, 1568, 1532, 1475, 1444, 1397, 1323, 1142, 1085, 1004, 828, 795, 758 cm^{-1} ; elemental analysis (%) calcd for $C_5H_5N_9O_{10}$ (351.15): C, 17.10; H, 1.44; N, 35.90; found: C, 17.52; H, 1.42; N, 35.64. The structure of **11** is supported by single crystal X-ray analysis.

3,4-Dinitro-N-(2,2,2-trinitroethyl)-1H-pyrazol-1-amine (12): White solid (225 mg, 67%). T_m 87 °C, onset T_{dec} 112 °C; 1H NMR: δ 8.44 (s, 1H), 7.24 (s, 1H), 4.98 (d, $J = 4.8$ Hz, 2H); ^{13}C NMR: δ 146.5, 134.3, 127.6, 126.6, 52.8; IR (KBr pellet): ν 3296, 3147, 3011, 2970, 2895, 1599, 1547, 1464, 1417, 1337, 1304, 1238, 1115, 1044, 893, 862, 804, 751 cm^{-1} ; ^{15}N NMR: δ -26.79, -26.90, -30.24 (t, $J = 2.03$ Hz), -81.25, -164.46, -295.13 (d, $J = 83.66$ Hz); elemental analysis (%) calcd for $C_5H_4N_8O_{10}$ (336.13): C, 17.87; H, 1.20; N, 33.34; found: C, 17.93; H, 1.15; N, 31.97.

4-Nitro-N-(2,2,2-trinitroethyl)-1H-pyrazol-1-amine (13): White solid (209 mg, 72%). T_m 109 °C, onset T_{dec} 129 °C; 1H NMR: δ 8.29 (s, 1H), 8.08 (s, 1H), 7.01 (s, 1H), 4.95 (s, $J = 4.8$ Hz, 2H); ^{13}C NMR: δ 135.6, 135.2, 131.0, 128.2, 53.3; IR (KBr pellet): ν 3258, 3160, 3119, 3007, 1594, 1532, 1403, 1317, 1225, 997, 966, 882, 790, 752 cm^{-1} ; elemental analysis (%) calcd for $C_5H_5N_7O_8$ (291.14): C, 20.63; H, 1.73; N, 33.68; found: C, 20.71; H, 1.68; N, 32.32.

3,4-Dinitro-1H-pyrazole-1,5-diamine (15): Triphenylphosphine (394 mg, 1.5 mmol) was added to a solution of 5-azido-3,4-dinitro-1H-pyrazol-1-amine (**8**, 214 mg, 1 mmol) in THF (8 ml) at 0 °C, and the resulting solution was stirred overnight at room temperature. The solvent was removed under reduced pressure and a mixture of ethanol (10mL) and 2M HCl (20 mL) was added to the residue. The reaction was stirred overnight at 50 °C. The resulting clear solution was concentrated under reduced pressure to remove most of the ethanol and then extracted with ethyl acetate (3 \times 20 mL). The combined organic phase was dried over Na_2SO_4 , filtered and the solvent was removed in *vacuo*. The residue was chromatographed on silica gel eluting with hexane/ethyl acetate (100:75) to give **15**. Pale yellow solid (143 mg, 76%). T_m 133°C, onset T_{dec} 275 °C; 1H NMR: δ 6.47 (s, 2H), 5.37 (s, 2H); ^{13}C NMR: δ 147.6, 146.3, 109.2; ^{15}N NMR: δ -23.13, -23.31, -97.85, -201.98, -308.27 (t, $J = 75.54$ Hz), -319.44 (t, $J = 93.78$ Hz); IR (KBr pellet): ν 3360, 3346, 1661, 1551, 1516, 1471, 1373, 1334, 1272, 949 cm^{-1} ; elemental analysis (%) calcd for $C_3H_4N_6O_4$ (188.03): 19.16; H, 2.14; N, 44.68; found: C, 19.27; H, 2.11; N, 44.18.

3,4-Dinitro- N^1 -(2,2,2-trinitroethyl)-1H-pyrazole-1,5-diamine (16): White solid (256 mg, 73%). Onset T_{dec} 113 °C; 1H NMR: δ 6.58 (s, 2H), 6.46 (s, 1H), 4.91 (d, $J = 4.8$ Hz, 2H); ^{13}C NMR: δ 147.7, 147.3, 127.7, 109.0, 52.7; ^{15}N NMR: δ -23.76, -23.88, -30.72, -106.99, -195.89, -309.50 (d, $J = 85.18$ Hz), -317.48 (t, $J = 94.30$ Hz); IR (KBr pellet): ν 3459, 3387, 3274, 3007, 1663, 1595, 1559, 1525, 1458, 1379, 1337, 1306, 1267, 1168, 1107, 825, 781 cm^{-1} ; elemental analysis (%) calcd for $C_5H_3N_9O_{10}$ (351.15): C, 17.10; H, 1.44; N, 35.90; found: C, 17.16; H, 1.38; N, 35.01.

3-Nitro-1H-1,2,4-triazol-1-amine (17): 3-Nitro-1H-1,2,4-triazol-1-amine (10 mmol) was added to aqueous ammonia (10 mL) and stirred at room temperature for 0.5h. Then the water was removed by blowing air over the liquid surface and the residue was dried in *vacuo*. Dimethylformamide (50 mL) was added to the ammonium salt and followed by the freshly prepared *O*-tosylhydroxylamine in CH_2Cl_2 (100 mL, prepared as above). The mixture was stirred at room temperature for 2 d. Then the solvent was removed by rotary evaporation and ethyl acetate (50 mL) was added. The white precipitate was filtered and ethyl acetate was removed to afford the crude product, which could be further purified by column chromatography diluting with hexane/ethyl acetate (40/100). Pale yellow solid (787 mg, 61%). T_m 139 °C, onset T_{dec} 324 °C; 1H NMR (d_6 -DMSO): δ 8.73 (s, 1H), 7.18 (s, 2H); ^{13}C NMR (d_6 -DMSO): δ 158.8, 144.8; IR (KBr pellet): ν 3332, 3278, 3208, 3132, 1647, 1555, 1506, 1414, 1309, 1195, 1032, 833 cm^{-1} ; elemental analysis (%) calcd for $C_2H_3N_5O_2$ (129.08): C, 18.61; H, 2.34; N, 54.26; found: C, 18.64; H, 2.28; N, 53.82.

3-Nitro-1H-1,2,4-triazole-1,5-diamine (18): A mixture of 3-nitro-1H-1,2,4-triazol-5-amine (387 mg, 3 mmol, 1 equiv), K_2CO_3 (4.15 g, 30 mmol, 10 equiv) and distilled water (20 mL) was

stirred at 60 °C. To the yellow solution, hydroxylamine-*O*-sulfonic acid (1.02 g, 9 mmol) was added over ten minutes, and the mixture was stirred overnight at 60 °C. The final aqueous solution was extracted by ethyl acetate (3×40 mL), and then the combined organic phase was dried over Na₂SO₄. The solvent was removed under reduced pressure to give the pure aminated product **18**. Yellow solid (138 mg, 32%). *T*_{dec} 275 °C; ¹H NMR (*d*₆-DMSO): δ 6.84 (s, 2H), 6.37, (s, 2H), ¹³C NMR (*d*₆-DMSO): δ 156.1, 155.5; IR (KBr pellet): ν 3424, 3339, 3229, 1672, 1627, 1557, 1516, 1446, 1404, 1314, 1142, 1087, 873, 793 cm⁻¹; elemental analysis (%) calcd for C₂H₄N₆O₂ (144.09): C, 16.67; H, 2.80; N, 58.32; found: C, 16.67; H, 2.80; N, 57.81.

3-Nitro-*N*-(2,2,2-trinitroethyl)-1H-1,2,4-triazol-1-amine (19): White solid (190 mg, 65%). *T*_{dec} 151 °C; ¹H NMR: δ 8.31 (s, 1H), 7.15 (s, 1H), 4.97 (s, 2H); IR (KBr pellet): 3254, 3154, 3015, 2976, 2886, 1606, 1557, 1508, 1418, 1317, 1300, 1194, 1107, 1015, 841, 801, 656 cm⁻¹; elemental analysis (%) calcd for C₄H₄N₈O₈ (292.12): C, 16.45; H, 1.38; N, 38.36; found: C, 16.54; H, 1.39; N, 37.29.

3-Nitro-*N*-(2,2,2-trinitroethyl)-1H-1,2,4-triazole-1,5-diamine (20): White solid (233 mg, 76%). *T*_{dec} 135 °C; ¹H NMR: δ 6.48 (s, 1H), 5.61 (s, 2H), 4.92 (s, 2H); IR (KBr pellet): 3525, 2422, 3252, 3006, 2925, 1649, 1603, 1559, 1410, 1299, 1163, 910, 854, 798, 719 cm⁻¹; elemental analysis (%) calcd for C₄H₅N₉O₈ (307.14): C, 15.64; H, 1.64; N, 41.04; found: C, 15.78; H, 1.63; N, 38.80.

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Table of Contents:

Diversified energetic groups are introduced into triazoles and pyrazoles giving rise to C-/N- bifunctionalized pyrazoles and triazoles, which are promising energetic materials.

