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ARTICLE

Versatile Functionalization of 3,5-Diamino-4-nitropyrazole for Promising Insensitive Energetic Compounds

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Variation of functional groups offers an efficient approach for tuning properties of materials such as thermal stability, and detonation performance while improving sensitivities to mechanical stimuli. Now versatile functionalization of 3,5-diamino-4-nitropyrazole involving the introduction of a tetrazole ring, or a guanyl group, or ring expansion is described. All of the compounds were fully characterized and some of them (**2**, **9** and **13**) were verified by single crystal X-ray diffraction. Based on their good thermal stabilities and high detonation performance as well as insensitive properties, they are potentially insensitive energetic compounds.

Introduction

In developing energetic materials, there is a great need for a balance between high performance/insensitive properties and environmental friendliness.[1] Benefitting from the merits of high nitrogen content, high heat of formation and green combustion gas (N_2), nitrogen-rich heterocyclic compounds have been investigated extensively and are found to be promising replacements for traditional explosives, such as 1,3,5-trinitrotoluene (TNT) and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX).[2-5]

Five-membered or six-membered nitrogen-rich heterocyclic rings, including tetrazole, triazole, pyrazole, furazan, tetrazine, triazine, et al., have emerged as attractive building blocks for construction of energetic materials. Among them, the pyrazole ring demonstrates that the presence of three catenated carbon atoms traditionally gives good thermal stability and insensitivity as well as easily modified energetic moieties.[6, 7] Pyrazole rings with energetic nitro and desensitizing amino functional groups and NH bonded to the pyrazole often result in versatile derivatives. 4-Amino-3,5-dinitropyrazole and 5-amino-3,4-dinitropyrazole are frequent precursors to many energetic compounds, such as oxidation to give full C-nitrated trinitropyrazole[8] and nitration to form 4-nitramino-3,5-dinitropyrazole with the former,[9] and ring expansion to form 4-amino-3,7-dinitro-[1,2,4]triazolo[5,1-*c*][1,2,4]triazine with 5-amino-3,4-dinitropyrazole.[10, 11]

Interestingly, 3,5-diamino-4-nitropyrazole with two amino groups and one NH on the pyrazole ring is expected to be a good precursor for preparation of high-performance energetic materials.[12] However, its energetic derivatives were not studied until our recent work involving a highly thermally stable fused compound[13] and a series of high-performance dinitramino substituted salts.[14] 3,5-Diamino-4-nitropyrazole was prepared first by a tedious method in 1976[15] and a convenient route was provided later.[16] In order to examine its chemical activities further and to search for some additional fascinating energetic compounds, we now describe some diverse reactions based on the amino group and the NH on the pyrazole ring. Several energetic compounds were synthesized and fully characterized. Most of them show good thermal stabilities and good detonation performance and have potential application in the field of insensitive energetic materials.

Results and discussion

Synthesis

The synthesis of 3,5-diamino-4-nitro-1-(1*H*-tetrazol-5-yl)pyrazole (**2**) resulted from the reaction of cyanogen azide with the sodium salt of **1**. The energetic salts **3**–**7** were prepared by the simple neutralization reaction of **2** and selected nitrogen-rich bases. Compound **2** was suspended in a mixture of water and methanol, the corresponding base was added and the suspension was heated at 60 °C for 2 h. The solvents were removed to give the new salts **3** **7**. The materials were purified by recrystallization from hot water (Scheme 1).

Reaction of **1** with gaseous HCl in methanol gave **8**, which was treated with cyanamide in ethanol at reflux for 12 h to form 3,5-diamino-1-guanyl-4-nitro-1,2,4-triazole hydrochloride (**9**). The structure is supported by ^1H, ^{13}N NMR and elemental analysis as well as single crystal X-ray structuring. However, the attempts to react **1** with cyanamide in dilute HCl did not result in product

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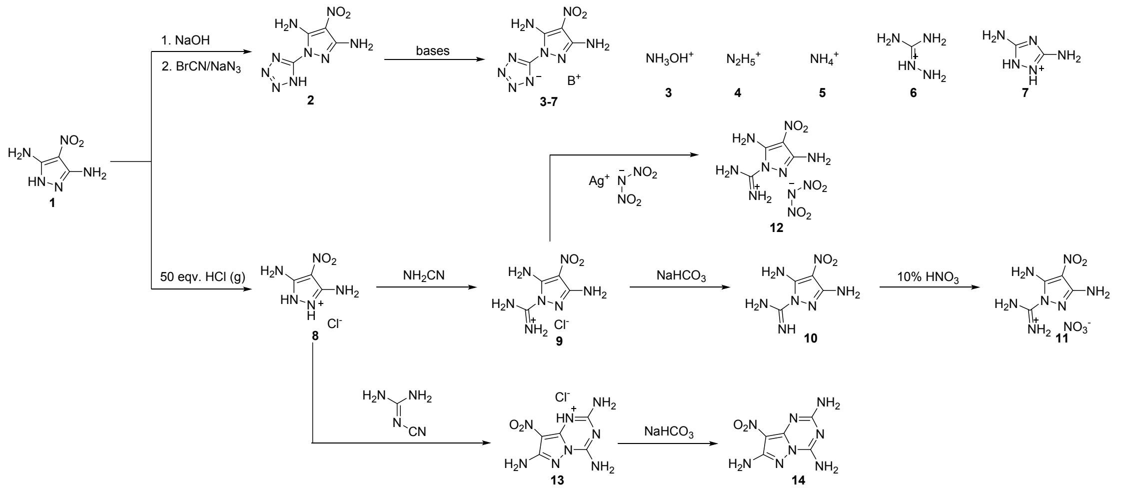


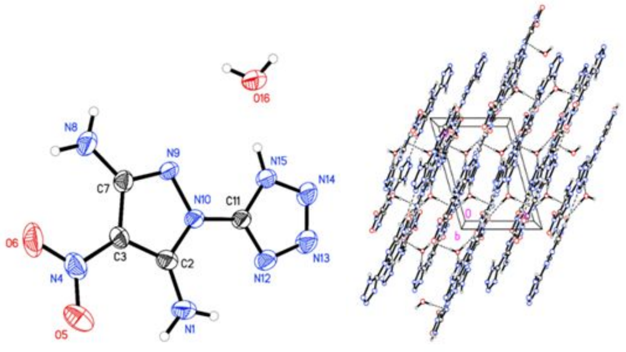
Scheme 1 Synthesis of energetic derivatives based on 3,5-diamino-4-nitropyrazole

9, only the starting material **1** remained. Neutralization of **9** with a saturated solution of sodium bicarbonate generated **10**. Further reaction of **10** with dilute HNO_3 gave 3,5-diamino-1-guanyl-4-nitro-1,2,4-triazole nitrate (**11**). 3,5-Diamino-1-guanyl-4-nitro-1,2,4-triazole dinitramide (**12**) was prepared by a 1:1 stoichiometric reaction of the monohydrochloride salt **9** and silver dinitramide in water.

When compound **8** was treated with dicyanamide in ethanol at reflux for 6 h, 8-nitropyrazolo[1,5-*a*][1,3,5]triazine-2,4,7-triamine hydrochloride (**13**) was isolated and confirmed by single crystal X-ray diffraction. However, only the starting material **1** was recovered when **1** was treated with dicyanamide in dilute HCl solution. The fused compound, 8-nitropyrazolo[1,5-*a*][1,3,5]triazine-2,4,7-triamine (**14**), was prepared by neutralization of **13** with sodium bicarbonate.

Single crystal X-ray diffraction analysis

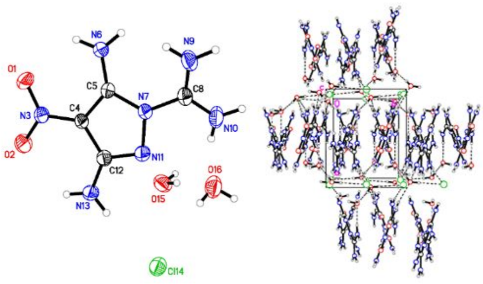
Compound **2** crystallizes as a monohydrate in the monoclinic *P*2$_1$/c space group with four formula units per unit cell and a crystal density of 1.693 g cm^{-3} at 293 K. Its molecular structure is shown in Fig. 1a. The bond lengths in the pyrazole ring and tetrazole ring are between typical single and double bonds and also are comparable to the reported structures.[17, 18] The bond length of N10-C11 is 1.371(2) Å. The two amino groups and the nitro group, as well as the pyrazole ring are nearly coplanar (torsion angles: N8-C7-N9-N10 = 179.48(15)°; C7-C3-N4-O6 = -2.3(3) °; N1-C2-C3-N4 = 1.7(3)°). The tetrazole ring is slightly twisted from the pyrazole ring with a torsion angle of C2-N10-C11-N15 = -169.77(16)°. In addition, the structure is dominated by an extensive hydrogen bonding network (Fig. 1b). The solvent water molecules also play an important role in forming hydrogen bonds with the nitrogen atom and the oxygen atoms (N15-H15···O16, O16-H16B···O6, and O16-H16A···N9).



(a) (b)

Fig.1 (a) Molecular structure of **2**; (b) Packing diagram of **2** viewed from *b* axis.

Compound **9** crystallizes as a dihydrate in the monoclinic *P*2$_1$/c space group with four formula units per unit cell and a crystal density of 1.602 g cm^{-3} at 296 K. Its molecular structure is shown in Fig. 2a. The bond length (1.298(3) Å) of C8-N10 is slightly shorter than that of C8-N9 (1.314(3) Å), indicating that the C8-N10 has some C=N double bond character. In comparison with the bond length (1.371(2) Å) of N10-C11 in **2**, the bond length of N7-C8 is 1.383(2) Å in **9**. Similarly, the two C-amino groups and nitro group are almost coplanar with the pyrazole ring (torsion angles: N(6)-C(5)-N(7)-N(11) = -176.53(18)°, O(2)-N(3)-C(4)-C(5) = 178.26(19)°, and C(5)-C(4)-C(12)-N(13) = -180.0(2)°). However, the guanyl group is a little twisted from the pyrazole ring with a torsion angle of C(5)-N(7)-C(8)-N(9) = 27.8(3)°. The packing diagram was not only extended by many hydrogen bonds but also stabilized by the N-H···Cl and O-H···Cl interactions (Fig. 2b). The details are given in the Electronic Supplementary Information (ESI).



(a) (b)

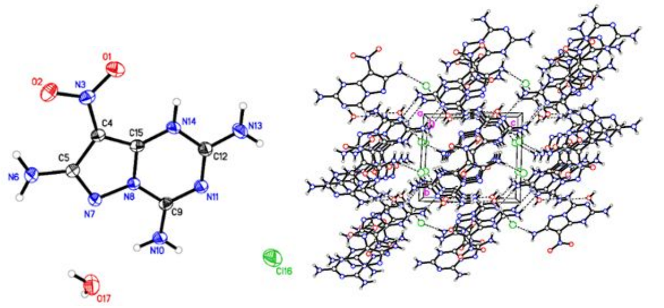
Fig.2 (a) Molecular structure of **9**; (b) Packing diagram of **2** viewed from *c* axis.

Table 1. Physical and detonation properties of the synthesized compounds in comparison with TATB and LLM-105

Compounds	T_d a) [°C]	ρ b) [g cm^{-3}]	$\Delta_f H$ c) [kJ mol^{-1}/kJ g^{-1}]	vD d) [m s^{-1}]	P e) [Gpa]	IS f) [J]	FS g) [N]
2	272	1.76	407.7/1.93	8257	25.9	30	360
3	187	1.78	445.0/1.82	8818	29.9	32	360
4	229	1.75	547.1/2.25	8801	28.9	35	360
5	251	1.70	399.1/1.75	8286	24.9	40	>360
6	224	1.69	485.5/1.70	8244	23.9	40	>360
7	287	1.72	337.7/1.03	8138	23.6	40	>360
10	200	1.72	127.6/0.69	8004	22.8	>40	>360
11	196	1.68	-483.3/-1.7	8002	23.8	32	360
12	148	1.75	462.8/1.58	8810	32.6	30	360
14	406	1.78	127.1/0.60	7789	21.8	>40	>360
TATB i)	350	1.93	-139.7/-0.54	8179	30.5	50	>360
LLM-105 i)	342	1.92	11/0.05	8639	31.7	20	360

a) Thermal decomposition temperature (onset) under nitrogen gas (DSC, 5 °C/min); b) Measured densities - gas pycnometer at room temperature; c) Calculated heat of formation; d) Calculated detonation velocity; e) Calculated detonation pressure; f) Impact sensitivity; g) Friction sensitivity; i) ref. 21.

Compound **13** crystallizes as a monohydrate in the triclinic *P*-1 space group with two formula units per unit cell and a crystal density of 1.737 g cm^{-3} at 296 K. Its molecular structure is shown in Fig. 3a. As can be seen, the nitrogen atom (N14) in the triazine ring is protonated. The torsion angles (O(1)-N(3)-C(4)-C(5) = 179.63(16)°, N(6)-C(5)-N(7)-N(8) = -177.83(16)°, N(10)-C(9)-N(11)-C(12) = 177.79(16)° , and N(13)-C(12)-N(14)-C(15) = -178.41(17)°) show that the nitro group and all the three amino groups are nearly coplanar with the fused backbone. Several hydrogen bonds were observed between chloride ions and nitrogen/oxygen atoms (Cl16···H6A–N6, Cl···H13A–N13, Cl16···H–O17). In addition, the nitrogen atoms (N6, N10 and N13) from the amino groups also form three kinds of hydrogen bonds with oxygen/nitrogen atoms (N6–H6B···O2, N10–H10B···O17, N13–H13A···N11).



(a) (b)

Fig.3 (a) Molecular structure of **13**; (b) Packing diagram of **13** viewed from *a* axis.

Physicochemical and energetic properties

The thermal behavior of the new compounds was determined by differential scanning calorimetry (DSC) in covered Al pans with a hole in the lid using a nitrogen flow of 50 mL min^{-1} at a heating rate of 5 °C min^{-1}. All of the compounds show good thermal stabilities (> 180 °C) except the dinitramide salt (**12**) which decomposes at 148 °C. The neutral fused compound (**14**) has the highest decomposition temperature of 406 °C. The C-N bonded biheterocyclic compound (**2**) also displays an excellent decomposition temperature of 270 °C. The corresponding salts (**3**-**7**) show lower decomposition temperatures than that of **2**, while the 3,5-diamino-1,2,4-triazole salt (**7**) decomposes at 287 °C. Compound **10** and its nitrate salt (**11**) decompose at 200 and 196 °C, respectively.

For all the new materials, the measured densities are between 1.69 g cm^{-3} and 1.78 g cm^{-3}. The heats of formation were calculated by the Gaussian 09 (revision E01) suite of programs[19] with isodesmic reactions. Due to the incorporation of the tetrazole ring, compounds **2**-**7** have positive heats of formation. However, the presence of water molecules in **11** results in a negative heat of formation. With the measured densities and calculated heats of formation, the detonation performances were calculated by using EXPLO6 v6.01 As seen in Table 1, the hydroxylammonium (**3**) and hydrazinium (**4**) salts have higher detonation velocities than either TATB or LLM-105 and their detonation pressures are close. The dinitroamide salt (**12**) shows good detonation velocity (8810 m s^{-1}) and detonation pressure (32.6 GPa).

For safety considerations, the sensitivities towards impact and friction were measured according to standard BAM techniques.[20] The impact sensitivity of **2** is 30 J, and its energetic salts exhibit low sensitivity values (32 J – 40 J). They also have low sensitivity to friction (360 N for **2** **4** and >360 N for **5** **7**). Compounds **10** and **14** are very insensitive with impact sensitivities > 40 J and the friction sensitivities > 360 N.

Conclusions

In conclusion, we have developed a family of energetic derivatives based on 3,5-diamino-4-nitropyrazole. The reaction of **1** and cyanogen bromide led to a C-N bonded tetrazole and pyrazole molecule (**2**). Its nitrogen-rich energetic salts (**3**-**7**) were also synthesized. Treatment of **1** with cyanamide/dicyanamide gave the guanyl substituted product (**9**) and ring-expansion product (**13**), respectively. Most of them show high thermal stability and good detonation performance. Among them, the hydroxylammonium (**7**) and hydrazinium (**8**) salts show better detonation velocities than TATB and LLM-105. Compound **14** has an extremely high decomposition temperature of 406 °C. Considering their low sensitivities and high thermal stabilities, they may find applications in the field of insensitive energetic materials.

Experimental section

Caution! Although we did not encounter any difficulties or explosions in the preparation of the target molecule, proper protective precautions (face shield, leather coat, gloves and ear plugs) should be used when scraping and transferring those compounds.

General Methods: ^1H and ^{13}C NMR spectra were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer operating at 300.13 and 75.48 MHz, respectively, by using d_6-DMSO as the solvent and locking solvent. The decomposition points were obtained on a differential scanning calorimeter (TA Instruments Company, Model: Q2000) at a scan rate of 5 °C min^{-1}. IR spectra were recorded on a FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films using KBr plates. Densities were measured at room temperature by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Elemental analyses were determined using a Vario Micro cube Elementar Analyser. The sensitivities were determined by using a BAM drop hammer and friction tester.

Computational Methods: The gas phase enthalpies of formation were calculated based on isodesmic reactions (ESI, Scheme S1). The enthalpy of reaction is obtained by combining the MP2/6–311++G** energy difference for the reactions, the scaled zero point energies (ZPE), values of thermal correction (HT), and other thermal factors. The solid-state heats of formation were calculated based on Trouton's rule according to equation (1) (*T* represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition).[22]

$$\Delta H_{sub} = 188 / Jmol^{-1}K^{-1} \times T \qquad (1)$$

For energetic salts, the solid-phase enthalpy of formation is obtained using a Born–Haber energy cycle.[23] For compounds which are hydrates ($\mathbf{7}\cdot H_2O$ and $\mathbf{11}\cdot 2H_2O$), the solid-phase enthalpy of formation is obtained by adding the gas phase heat of formation of the anhydrous compound to that of water (-241.8 kJ mol^{-1}).[24]

Crystal Structure Analysis

A clear yellow block crystal ($\mathbf{2}\cdot H_2O$) of dimensions 0.362 × 0.212 × 0.085 mm^3, a clear yellow needle crystal ($\mathbf{9}\cdot 2H_2O$) of dimensions 0.226 × 0.036 × 0.036 mm^3, and a clear colorless block crystal ($\mathbf{13}\cdot H_2O$) of dimensions 0.308 × 0.223 × 0.060 mm^3 were mounted on a MiteGen MicroMesh using a small amount of Cargille immersion oil. 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$_\alpha$ radiation (λ = 0.71073 Å). Data were collected at room temperature (20 °C).

Data collection was carried out and the unit cell was initially refined using *APEX3* [v2015.5-2].[25] Data reduction was performed using *SAINT* [v8.34A][26] and *XPREP* [v2014/2].[27] Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2014/2].[28] The structure was solved and refined with the aid of the program SHELXL-2014/7.[29] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. Hydrogen atoms were located from difference electron-density maps and added using a riding model.

Synthesis of 3,5-diamino-4-nitro-1-(1*H*-tetrazol-5-yl)pyrazole (2)

Cyanogen bromide (2.65 g, 25 mmol) was dissolved in dry acetonitrile (50 mL) at 0 °C, then sodium azide (6.5 g, 100 mmol) was added to the solution and the reaction mixture was stirred for 4 h at 0 5 °C. The inorganic salt was removed by filtration and the filtrate was added to an aqueous solution of **1** (1.43 g, 10 mmol) which had been treated with an equivalent of sodium hydroxide. After stirring for 20 h at room temperature, the solvent was removed by air. The residue was added to water (50 mL) and then adjusted to pH = 1 with concentrated hydrochloric acid. The resulting precipitate was collected by filtration and washed twice with cold water (20 mL × 2) and recrystallized from hot water to give a yellow solid (**2**).

2: Yellow solid (1.52 g, yield: 72%). T_m: 133 °C. $T_{d\ (onset)}$: 272 °C. ^1H NMR (d_6-DMSO): 8.15 (s, 4H) ppm. ^{13}C NMR (d_6-DMSO): δ 152.6, 151.2, 146.4, 108.4 ppm. IR (KBr): v = 3377, 3274, 1620, 1578, 1497, 1401, 1234, 1128, 1059, 1028, 993, 802, 767, 738, 652 cm^{-1}. Elemental analysis for $C_4H_5N_9O_2$ (211.14): Calcd C 22.75, H 2.39, N 59.70 %. Found: C 22.57, H 2.67, N 58.46 %.

General procedures for synthesis of energetic salts 3–7

Compound **2** (0.42 g, 2.0 mmol) was added to a solution of the corresponding base (2.0 mmol) in a mixture of H_2O (10 mL) and methanol (10 mL), the reaction mixture was stirred at 60 °C for 2 h. The solution was then dried by air and the residue was recrystallized from H_2O to give the pure product.

Hydroxylammonium 3,5-diamino-4-nitro-1-(1*H*-tetrazol-5-yl)pyrazolate (3): Yellow solid (0.39 g, yield: 80%). $T_{d\ (onset)}$: 187 °C. ^{1}H NMR (d_6-DMSO): 8.82 (br, 4H), 8.07 (s, 2H), 6.14 (s, 2H) ppm. ^{13}C NMR (d_6-DMSO): δ 159.0, 149.7, 144.4, 108.1 ppm. IR (KBr): v = 3471, 3407, 3366, 3267, 1617, 1565, 1493, 1408, 1357, 1224, 1195, 1144, 1073, 996, 843, 804, 770 cm^{-1}. Elemental analysis for $C_4H_8N_{10}O_3$ (244.17): Calcd C 19.68, H 3.30, N 57.36 %. Found: C 20.08, H 3.55, N 56.93 %.

Hydrazinium 3,5-diamino-4-nitro-1-(1*H*-tetrazol-5-yl)pyrazolate (4): Yellow solid (0.49 g, yield: 85%). $T_{d\ (onset)}$: 229 °C. ^{1}H NMR (d_6-DMSO): 8.07 (s, 2H), 7.17 (br, 5H), 6.13 (s, 2H) ppm. ^{13}C NMR (d_6-DMSO): δ 159.1, 149.6, 144.4, 108.1 ppm. IR (KBr): v = 3431, 3328, 3175, 1628, 1578, 1543, 1510, 1403, 1377, 1277, 1221, 1189, 1152, 1099, 963, 814, 768 cm^{-1}. Elemental analysis for $C_4H_9N_{11}O_2$ (243.19): Calcd C 19.76, H 3.73, N 63.36 %. Found: C 20.39, H 3.71, N 61.29 %.

Ammonium 3,5-diamino-4-nitro-1-(1*H*-tetrazol-5-yl)pyrazolate (5): Yellow solid (0.37 g, yield: 82%). $T_{d\ (onset)}$: 251 °C. ^{1}H NMR (d_6-DMSO): 8.06 (s, 2H), 7.19 (s, 4H), 6.11 (s, 2H) ppm. ^{13}C NMR (d_6-DMSO): δ 159.0, 149.7, 144.4, 108.1 ppm. IR (KBr): v = 3432, 3312, 3174, 2855, 1623, 1572, 1543, 1511, 1433, 1410, 1376, 1227, 1171, 1075, 1018, 809, 768, 738, 656 cm^{-1}. Elemental analysis for $C_4H_8N_{10}O_2$ (228.17): Calcd C 21.06, H 3.53, N 61.39 %. Found: C 21.07, H 3.58, N 60.10 %.

Aminoguanidinium 3,5-diamino-4-nitro-1-(1*H*-tetrazol-5-yl)pyrazolate (6): Yellow solid (0.44 g, yield: 78%). $T_{d\ (onset)}$: 224 °C. ^{1}H NMR (d_6-DMSO): 8.70 (s, 1H), 8.07 (s, 2H), 7.35 (s, 2H), 6.88 (s, 2H), 6.15 (s, 2H), 4.70 (s, 2H) ppm. ^{13}C NMR (d_6-DMSO): δ 159.0, 158.8, 149.7, 144.4, 108.1 ppm. IR (KBr): v = 3446, 3305, 1632, 1567, 1516, 1436, 1402, 1382, 1227, 1160, 1014, 848, 815, 769, 735, 634 cm^{-1}. Elemental analysis for $C_5H_{11}N_{13}O_2$ (285.23): Calcd C 21.05, H 3.89, N 63.84 %. Found: C 21.24, H 3.77, N 61.56 %.

3,5-Diamino-1,2,4-triazolinium 3,5-diamino-4-nitro-1-(1*H*-tetrazol-5-yl)pyrazolate monohydrate (7·H$_2$O): Yellow solid (0.47 g, yield: 72%). $T_{d\ (onset)}$: 287 °C. ^{1}H NMR (d_6-DMSO): 8.07 (s, 2H), 7.52 (br), 6.12 (s, 2H) ppm. ^{13}C NMR (d_6-DMSO): δ 158.7, 152.2, 149.7, 144.4, 108.2 ppm. IR (KBr): v = 3471, 3418, 3274, 3122, 1708, 1661, 1634, 1577, 1539, 1500, 1442, 1227, 1198, 1166, 1055, 1012, 836, 794, 767, 736, 661, 594 cm^{-1}. Elemental analysis for $C_6H_{12}N_{14}O_3$ (328.25): Calcd C 21.95, H 3.68, N 59.74 %. Found: C 22.57, H 3.50, N 60.33 %.

Synthesis of **9**

Compound **8**[13] (1.38 g, 7.68 mmol) was suspended in ethanol (20 mL) and cyanamide (0.51 g, 12.1 mmol) was added, the reaction mixture was heated to reflux and stirred for 12 h. After cooling to room temperauture, the solid was collected by filtration and washed with ethanol (5 mL) and diethyl ether (5 mL).

9: Yellow solid (1.28 g, yield: 75%). T_m: 92 °C. $T_{d\ (onset)}$: 213 °C. ^{1}H NMR (d_6-DMSO): 9.12 (s, 4H), 6.45 (s, 4H) ppm. ^{13}C NMR (d_6-DMSO): δ 152.8, 150.8, 148.2, 108.9 ppm. IR (KBr): v = 3446, 3399, 3311, 1670, 1624, 1561, 1509, 1385, 1189, 1174, 1146, 1070, 805, 770 cm^{-1}. Elemental analysis for $C_4H_8ClN_7O_2$ (221.61): Calcd C 21.68, H 3.64, N 44.24 %. Found: C 21.83, H 3.46, N 44.85 %.

Synthesis of **10**

Compound **9** (1.11 g, 5.0 mmol) was suspended in water (15 mL) and saturated sodium bicarbonate solution was added to neutralize the solution, after stirred another 15 min, the solid was collected by filtration and washed with water (5 mL) and dried in air.

10: Yellow solid (0.87 g, yield: 94%). T_m: 198 °C. $T_{d\ (onset)}$: 200 °C. ^{1}H NMR (d_6-DMSO): 9.99 (s, 1H), 8.13 (s, 1H), 6.82 (s, 2H), 6.18 (s, 2H) ppm. ^{13}C NMR (d_6-DMSO): δ 153.4, 151.0, 149.4, 107.9 ppm. IR (KBr): v = 3476, 3376, 3313, 1661, 1621, 1558, 1476, 1386, 1347, 1300, 1232, 1191, 1173, 1142, 1070, 896, 828, 770, 754, 705, 627 cm^{-1}. Elemental analysis for $C_4H_7N_7O_2$ (185.14): Calcd C 25.95, H 3.81, N 52.96 %. Found: C 26.04, H 3.79, N 52.78 %.

Synthesis of **11·2H$_2$O**

Compound **10** (0.37 g, 2.0 mmol) was added 10% HNO_3 (2 mL), after stirring for an additional 30 min at room temperature, the reaction mixture was dried by air and recrystallized with methanol and water.

11·2H$_2$O: Yellow solid (0.45 g, yield: 80%). T_m: 101 °C. $T_{d\ (onset)}$: 196 °C. ^{1}H NMR (d_6-DMSO): 9.01 (br), 6.44 (s, 2H) ppm. ^{13}C NMR (d_6-DMSO): δ 152.5, 150.7, 148.1, 108.8 ppm. IR (KBr): v = 3513, 3463, 3359, 1729, 1663, 1583, 1531, 1494, 1385, 1348, 1237, 1178, 1150, 1064, 815, 738, 712, 676, 638 cm^{-1}. Elemental analysis for $C_4H_{12}N_8O_7$ (284.19): Calcd C 16.91, H 4.26, N 39.43 %. Found: C 16.77, H 4.01, N 38.70 %.

Synthesis of **12**

Compound **9** (0.44 g, 2.0 mmol) was suspended to water (20 mL), then silver dinitramide (0.42 g, 2.0 mmol) was added. The reaction mixture was stirred for 1 h. After filtration, the filtrate was dried in air and the residue was recrystallized with water and methanol.

12: Yellow solid (0.50 g, yield: 85%). T_m: 99 °C. $T_{d\ (onset)}$: 148 °C. ^{1}H NMR (d_6-DMSO): 8.58 (br), 6.38 (s, 2H) ppm. ^{13}C NMR (d_6-DMSO): δ 152.7, 150.4, 148.9, 108.6 ppm. IR (KBr): v = 3515, 1363, 3408, 3358, 1728, 1655, 1580, 1534, 1496, 1388, 1349, 1238, 1178, 1064, 1004, 815, 768, 734, 712, 676, 638 cm^{-1}. Elemental analysis for $C_4H_8N_{10}O_6$ (292.17): Calcd C 16.44, H 2.76, N 47.94 %. Found: C 16.32, H 2.77, N 47.15 %.

Synthesis of **13**

Compound **8**[13] (0.54 g, 3.0 mmol) was suspended in ethanol (15 mL) and dicyandiamide (0.33 g, 4.0 mmol) was added, the reaction mixture was heated to reflux and stirred for 6 h. After cooling down to room temperauture, the solid was collected by filtration and washed with ethanol (5 mL) and diethyl ether (5 mL).

13: Yellow solid (0.59 g, yield: 80%). T_m: 152 °C. $T_{d\ (onset)}$: 401 °C. ^{1}H NMR (d_6-DMSO): 8.89 (s, 1H), 8.12 (s, 1H), 6.68 (br) ppm. ^{13}C NMR (d_6-DMSO): δ 158.0, 152.7, 149.2, 144.3, 108.6 ppm. IR (KBr): v = 3505, 3369, 3263, 3140, 1679, 1641, 1517, 1550, 1507, 1465, 1397, 1235, 1200, 1086, 848, 790, 765, 743, 709 cm^{-1}. Elemental analysis for $C_5H_7ClN_8O_2$ (246.61): Calcd C 24.35, H 2.86, N 45.44 %. Found: C 24.45, H 2.86, N 45.87 %.

Synthesis of **14**

Compound **13** (1.23 g, 5.0 mmol) was suspended in water (15 mL) and saturated sodium bicarbonate solution was added to neutralize the solution, after stirred another 30 min, the solid was collected by filtration and washed with water (5 mL) and dried in air.

14: Yellow solid (1.0 g, yield: 96%). $T_{d\ (onset)}$: 406 ^oC. ^1H NMR (d_6-DMSO): 8.13 (s, 1H), 7.43 (s, 2H), 7.16 (s, 1H), 6.57 (s, 2H) ppm. ^{13}C NMR (d_6-DMSO): δ 162.1, 153.5, 149.5, 148.7, 108.1 ppm. IR (KBr): v = 3482, 3439, 3213, 1636, 1561, 1502, 1378, 1241, 1209, 1172, 1087, 773 cm^{-1}. Elemental analysis for $C_5H_6N_8O_2$ (210.15): Calcd C 28.58, H 2.88, N 53.32 %. Found: C 28.85, H 3.05, N 52.80 %.

Conflicts of interest

There are no conflicts to declare.

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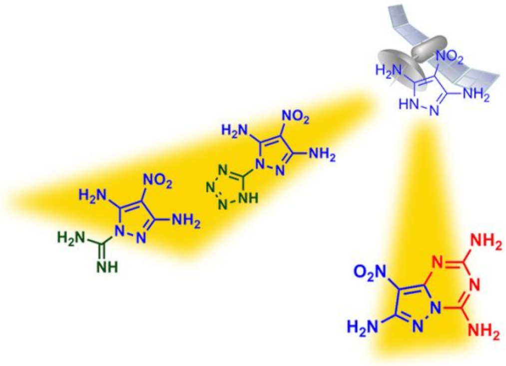

Energetic derivatives based on 3,5-diamino-4-nitropyrazole via diversified functionalization strategies show high thermal stability and good detonation performance.