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Research Article

Pushing the Limit of Nitro Groups on a Pyrazole Ring with Energy-Stability Balance

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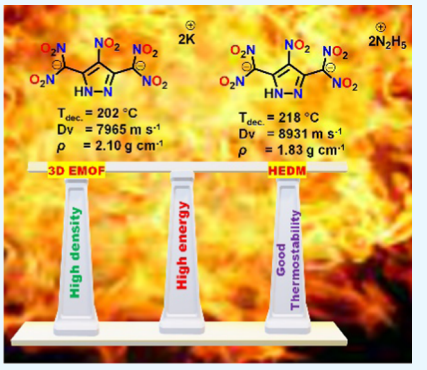
ABSTRACT: Polynitro compounds exhibit high density and good oxygen balance, which are desirable for energetic material applications, but their syntheses are often very challenging. Now, the design and syntheses of a new three-dimensional (3D) energetic metal−organic framework (EMOF) and high-energy-density materials (HEDMs) with good thermal stabilities and detonation properties based on a polynitro pyrazole are reported. Dipotassium 3,5-bis(dinitromethyl)-4-nitro-1*H*-pyrazole (**5**) exhibits a 3D EMOF structure with good thermal stability (202 °C), a high density of 2.15 g cm^{-3} at 100 K (2.10 g cm^{-3} at 298 K) in combination with superior detonation performance (D_v = 7965 m s^{-1}, P = 29.3 GPa). Dihydrazinium 3,5-bis(dinitromethyl)-4-nitro-1*H*-pyrazole (**7**) exhibits a good density of 1.88 g cm^{-3} at 100 K (1.83 g cm^{-3} at 298 K) and superior thermal stability (218 °C), owing to the presence of 3D hydrogen-bonding networks. Its detonation velocity (8931 m s^{-1}) and detonation pressure (35.9 GPa) are considerably superior to those of 1,3,5-trinitro-1,3,5-triazine (RDX). The results highlight the syntheses of a 3D EMOF (**5**) and HEDM (**7**) with five nitro groups as potential energetic materials.



KEYWORDS: *energetic MOF, high-energy-density materials, polynitro, pyrazole, energetic materials*

INTRODUCTION

Incorporation of nitro groups into molecules represents the most reliable method to increase power in energetic compounds.[1,2] This strategy has gained attention to enhance the density and oxygen balance of azole compounds for the development of high-energy-density materials (HEDMs).[3−5] Consequently, several polynitro compounds based on different azole rings, such as furoxan, triazole, and tetrazole, which contain explosophores, such as dinitromethyl and trinitromethyl groups, have been reported (Figure 1).[6−8] However, the limited scope of the application of these materials arises because of complications related to their thermal stability and sensitivity to external stimuli.[9] The thermal stability of a compound decreases with an increase in the number of nitro groups. For example, heterocycles[10,11] **i** and **ii**, which contain four nitro groups, decompose at ∼200 °C, whereas heterocycle[12] **iii** with six nitro moieties decomposes at ∼100 °C (Figure 1a). Unfortunately, heterocycle **iv** having six nitro groups is found to be too unstable to be characterized.[13] Therefore, the development of stable, high-energy polynitro compounds is a challenge.

The spectacular development of metal−organic frameworks (MOFs) has drawn broad interest from many research fields including energetic materials and is encouraging the emergence of new energetic metal−organic frameworks (EMOFs).[14−17] The EMOFs typically consist of one- and two-dimensional (1D and 2D) structures formed by the coordination of nitrogen-rich ligands and metal ions.[18,19] Recently, three-dimensional (3D) EMOFs have attracted considerable interest owing to their rigid structures and high densities.[20,21] The coordination of metal ions with the nitro groups and active protons of azoles is a useful strategy to realize high-density 3D EMOFs.[22] Recently, several groups reported the syntheses of EMOFs based on dinitromethyl- or trinitromethyl-functionalized azole rings (Figure 1b).[23] However, thermal stabilities of these EMOFs decrease with the increase in the number of nitro groups. Therefore, it is of significant interest to design and synthesize 3D EMOFs based on nitro-functionalized azole rings.

To obtain polynitro compounds with energy-stability balance, the combination of thermally stable azole rings bearing nitro groups as well as their easy functionalization is the key point and prerequisite. Pyrazole is an excellent building block for the generation of HEDMs due to its good thermal stability and low sensitivity.[24,25] Recently, it has been shown that the pyrazole ring can be linked with different nitrogen-rich heterocycles to achieve improved properties.[26,27] Nitro-substituted pyrazole derivatives further demonstrate the importance of achieving high density and good detonation properties (Figure 1c).[28−30] Examples of 3D EMOFs and HEDMs based on pyrazole bearing more than four nitro groups are rare and challenging (Figure

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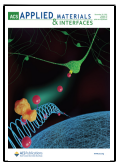


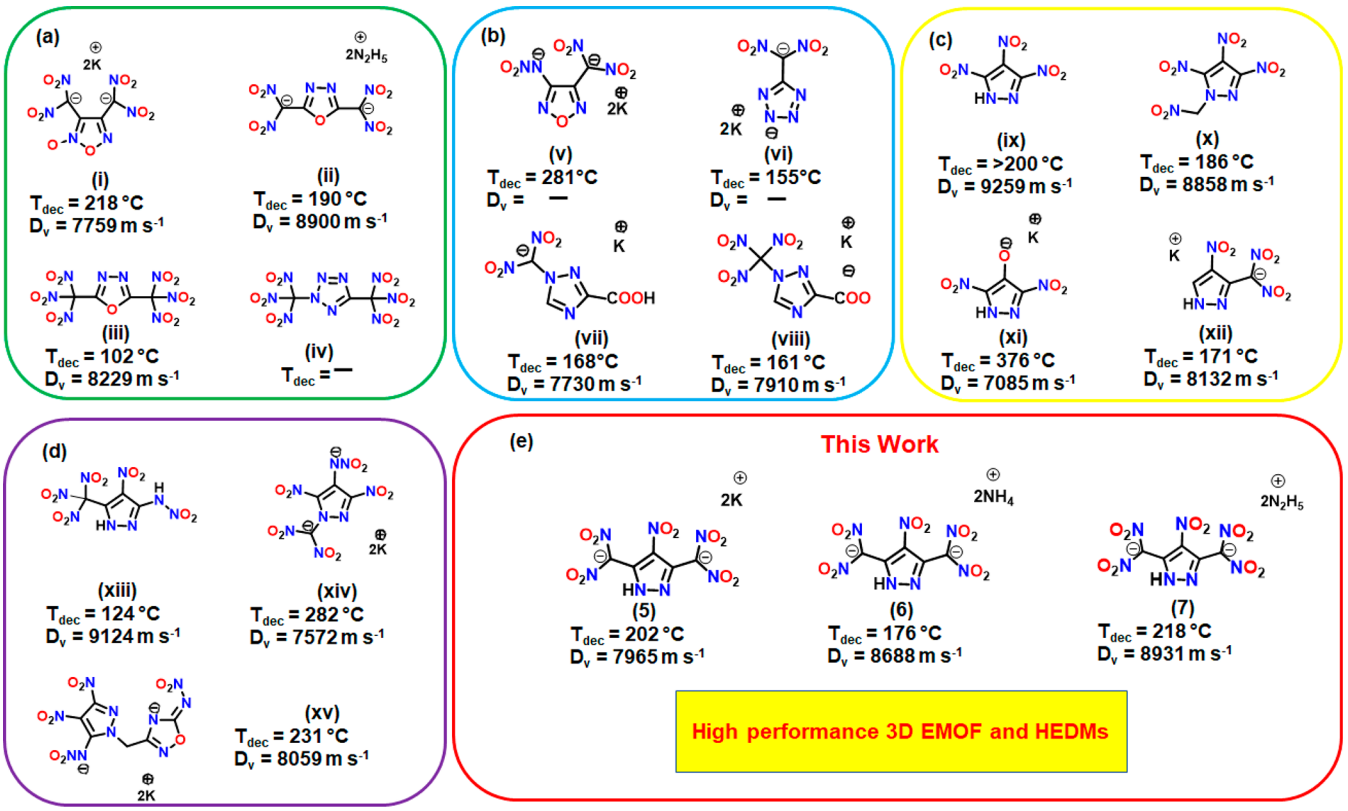
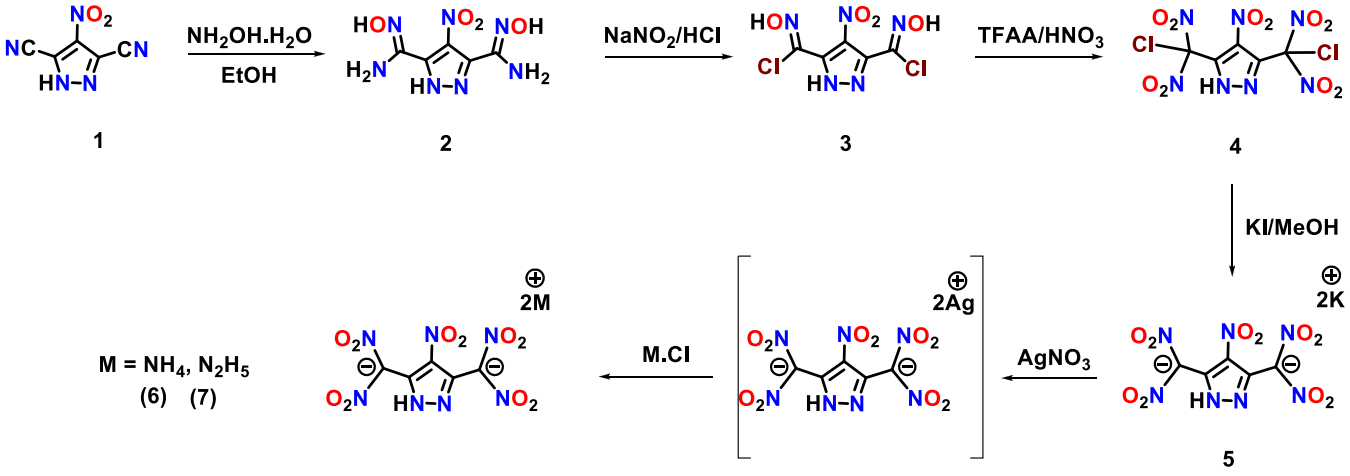


Figure 1. (a) Polynitro compounds based on different heterocyclic rings. (b) Reported potassium energetic metal−organic frameworks (EMOFs) with different heterocyclic rings. (c) Polynitro compounds based on the pyrazole ring. (d) Reported potassium EMOFs with polynitro pyrazole ring. (e) Compounds reported in this work.

Scheme 1. Synthesis of Dipotassium 3,5-Bis(dinitromethyl)-4-nitro-1*H*-pyrazole (5), Diammonium 3,5-Bis(dinitromethyl)-4-nitro-1*H*-pyrazole (6), and Dihydrazinium 3,5-Bis(dinitromethyl)-4-nitro-1*H*-pyrazole (7)



1d).[31−34] Aiming to push the limit of nitro groups on a heterocycle, we now report the synthesis and characterization of dipotassium 3,5-bis(dinitromethyl)-4-nitro-1*H*-pyrazole (**5**), diammonium 3,5-bis(dinitromethyl)-4-nitro-1*H*-pyrazole (**6**), and dihydrazinium 3,5-bis(dinitromethyl)-4-nitro-1*H*-pyrazole (**7**), bearing five nitro groups.

RESULTS AND DISCUSSION

Dipotassium 3,5-bis(dinitromethyl)-4-nitro-1*H*-pyrazole (**5**) was obtained in four steps from the dinitrile derivative **1** (Scheme 1). The reaction of compound **1** with hydroxylamine (50% in water) results in the formation of the diamidooxime derivative **2**, which can be diazotized with $NaNO_2$/HCl to give **3**. Compound **4** was synthesized by the reaction of **3** with trifluoroacetic acid anhydride and 100% nitric acid. Compound **4** was reacted with KI in methanol to give **5** as a light-yellow solid. The energetic salts, diammonium 3,5-bis(dinitromethyl)-4-nitro-1*H*-pyrazole (**6**) and dihydrazinium 3,5-bis(dinitromethyl)-4-nitro-1*H*-pyrazole (**7**), were obtained by reacting the silver salt with ammonium chloride and hydrazine monochloride, respectively (Scheme 1).

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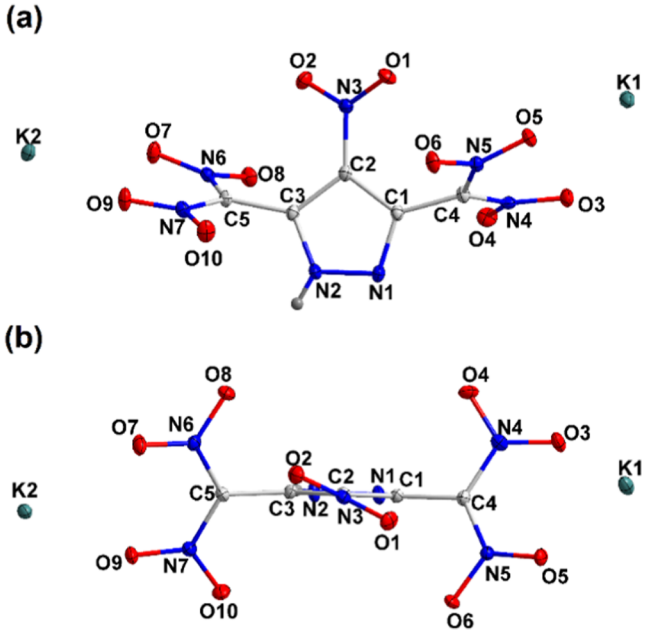

Figure 2. (a, b) Thermal ellipsoid (50%) plot and tagging scheme for **5**.

All compounds were characterized by NMR spectroscopy (^{1}H and ^{13}C), infrared spectroscopy (IR), and elemental analysis. The synthesis and characterization details for compounds **2**−**7** are given in the Supporting Information (SI). The structures of **5** and **7** were further confirmed by single-crystal X-ray diffraction (SC-XRD). Single crystals suitable for SC-XRD were obtained for **5** and **7** by slow evaporation of their saturated solutions in water. Crystallographic data are provided in the SI. Compound **5** crystallizes in the orthorhombic space group $Pna2_1$ with a calculated density of 2.153 g cm^{-3} at 100 K (Figure 2). In compound **5**, the bond distances between carbon and nitrogen atoms of C−$(NO_2)_2$ groups (N4−C4, 1.393(3), N5−C4, 1.366(3), N6−C5, 1.383(3), and N7−C5, 1.390(3)) are shorter than the C−NO_2 bond (N3−C2, 1.411(3)). The carbon and nitrogen atoms of the pyrazole are coplanar together with the carbon atoms of the dinitromethyl groups, with nitro groups located on each side of the pyrazole (Figure 2b). The torsion angles (N1−C1−C2−N3 (177.3°), N1−C1−C2−C3 (−0.2°), and N2−N1−C1−C4 (−179.2°)) approach ±180 and ±0°, which demonstrate that the pyrazole ring is nearly coplanar with the carbon atoms of the dinitromethyl moieties. The crystal packing of compound **5** is shown in Figure 3a,b. Due to the presence of many coordination bonds, compound **5** exists in a 3D MOF structure. As shown in Figure 3b, each dianion form is surrounded by several potassium cations through a coordination bond. The distance between an O-atom and the K-ions ranges from 2.669 to 3.121 Å. The distance between the pyrazole nitrogen (N1) and potassium ion is found to be 3.165 Å.

Compound **7** crystallizes in the triclinic space group $P\bar{1}$ with two dianions and four hydrazinium cations ($Z = 2$) in each unit cell (Figure 4). The calculated density of compound **7** at 100 K is 1.878 g cm^{-3}. The bond distances between carbon and nitrogen atoms of C−$(NO_2)_2$ groups (N4−C4, 1.370(3), N5−C4, 1.403(3), N6−C5, 1.387(3), and N7−C5, 1.369(3)) are shorter than the C−NO_2 bond (N3−C2, 1.428(3)). Similar to compound **5**, the carbon and nitrogen atoms of the pyrazole ring in compound **7** are coplanar with the carbon atoms of the dinitromethyl groups, with torsion angles N1−N2−C3−C5 = 179.0°, N1−C1−C2−C3 = −0.4°, and N2−N1−C1−C4 = −178.6°, respectively.

The presence of electronegative oxygen atoms in the dianion provides more opportunity for the cations to gather around it to form strong intermolecular contacts. The hydrazinium cation increases the intermolecular contacts, in particular, the hydrogen bonding formed by N−H···O or N−H···N interactions. Each dianion is stabilized by the hydrogen bonds from the surrounding hydrazinium cations to form a 3D network (Figure 5a,b). The hydrogen bonds and their lengths are given in the Supporting Information (Table S9). Due to the extensive 3D H-bonding networks, compound **7** exhibits a good crystal density.

Pyrazoles having an NH proton undergoes nonstoppable prototropic transformations. As a result, the free proton of the pyrazole ring is difficult to observe in ^{1}H NMR.[35−37] Interestingly, in the ^{1}H NMR spectrum of **5**, a peak at 13.7 ppm was assigned to the fixed proton of the pyrazole (Figure 6a). In addition, five characteristic peaks corresponding to the five carbon atoms are observed in the ^{13}C NMR (Figure 6b). This is due to the coordination between the ring nitrogen and potassium atoms, which results in blocking of the NH proton exchange (proton-locking). In contrast to **5**, compounds **6** and **7** show no NH proton in ^{1}H NMR spectra (Figure 6c,e). Moreover, compounds **6** and **7** show the three characteristic peaks of five carbons atoms in the ^{13}C NMR (Figure 6d,f). This is due to the axial symmetric structure of **6** and **7**, which is a result of nonstoppable prototropic tautomerism. In compounds **6** and **7**, the broad peaks arising from the NH signals corresponding to ammonium and hydrazinium group are observed at ∼7.18 and 7.80 ppm, respectively (Figure 6c,e). In addition, the chemical environments of different nitro groups were determined using ^{14}N NMR. A broad peak of five nitro

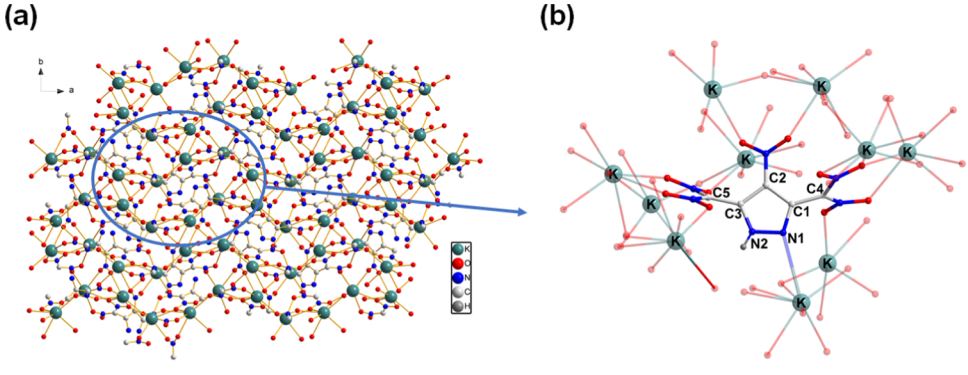

Figure 3. (a) Packing diagram of **5**. (b) Coordination diagram between the dianion and potassium atoms.

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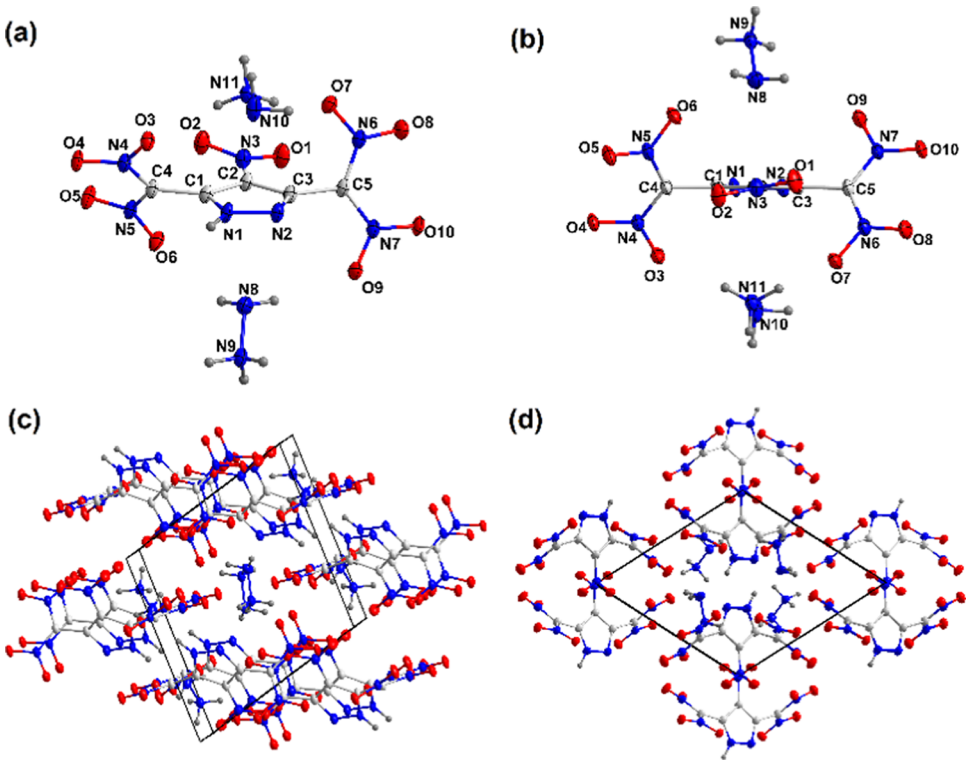

Figure 4. (a, b) Thermal ellipsoid (50%) plot and tagging scheme for **7**. (c, d) Packing diagrams of **7**.

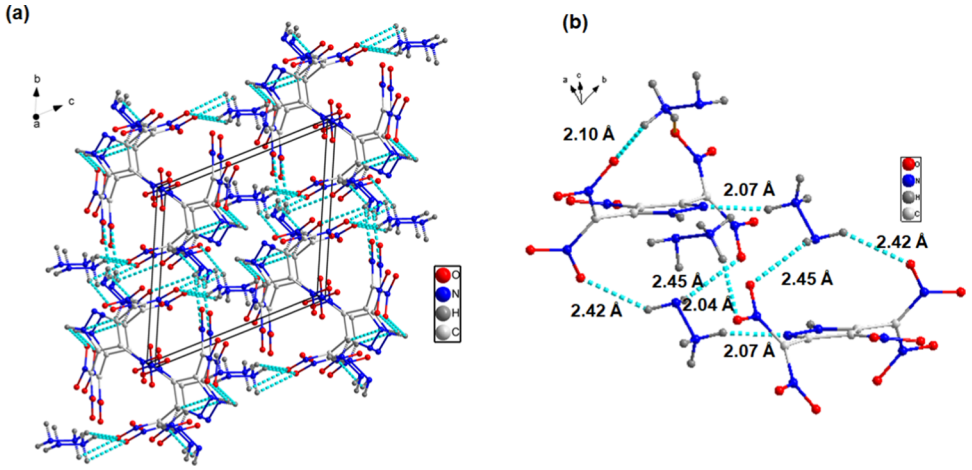

Figure 5. (a) 3D intermolecular hydrogen bonding (dotted lines) in the crystal structure of **7**. (b) Hydrogen bonds around the cation and anion in **7** (dotted lines).

groups is observed in **5**, **6**, and **7** at ∼−18.01, −22.73, and −22.95, respectively (Figures S11−S13).

The thermal behavior of **5**−**7** was explored using differential scanning calorimetry (DSC) at a heating rate of 5 °C min^{-1} (Figures S1−S3). They decompose (onset temperature) without melting at 202 °C (**5**), 176 °C (**6**), and 218 °C (**7**), respectively (Table 1). The densities were measured using a gas pycnometer at 25 °C and are 2.10 g cm^{-3} (**5**), 1.85 g cm^{-3} (**6**), and 1.83 g cm^{-3} (**7**), respectively (Table 1). To study the energetic properties of compounds **5**−**7**, the molar enthalpies of formation were calculated using isodesmic reactions with the Gaussian 03 (revision D.01) suite of programs. Compounds **5** and **6** have negative HOFs of −1.19 and −0.61 kJ g^{-1}, respectively, while compound **7** has a positive HOF of 0.29 kJ g^{-1}. The values of calculated HOFs and pycnometer-measured densities are used to calculate the detonation properties of compounds **5**−**7** (Table 1). The detonation velocities (calculated) are between 7965 and 8931 m s^{-1}, and detonation pressures (calculated) range from 29.3 to 35.9 GPa.

The detonation velocity and detonation pressure (8931 m s^{-1}, 35.9 GPa) of compound **7** are superior to 1,3,5-trinitro-1,3,5-triazine (RDX) (8795 m s^{-1}, 34.9 GPa) and the previously reported HEDMs **i**, **ii**, and **iii** (Figure 1) based on azole rings (Table 1). The IS and FS for **5**−**7** were measured using BAM standard methods. The new salts exhibit a sensitivity of impact values between 6 and 10 J and a sensitivity of friction values from 40 to 120 N. While **5** is sensitive toward impact and friction (IS 6 J, FS 40 N), **6** and **7** have IS of 10 and 8 J, respectively, and FS of 120 N, which are comparable to RDX (Table 1).

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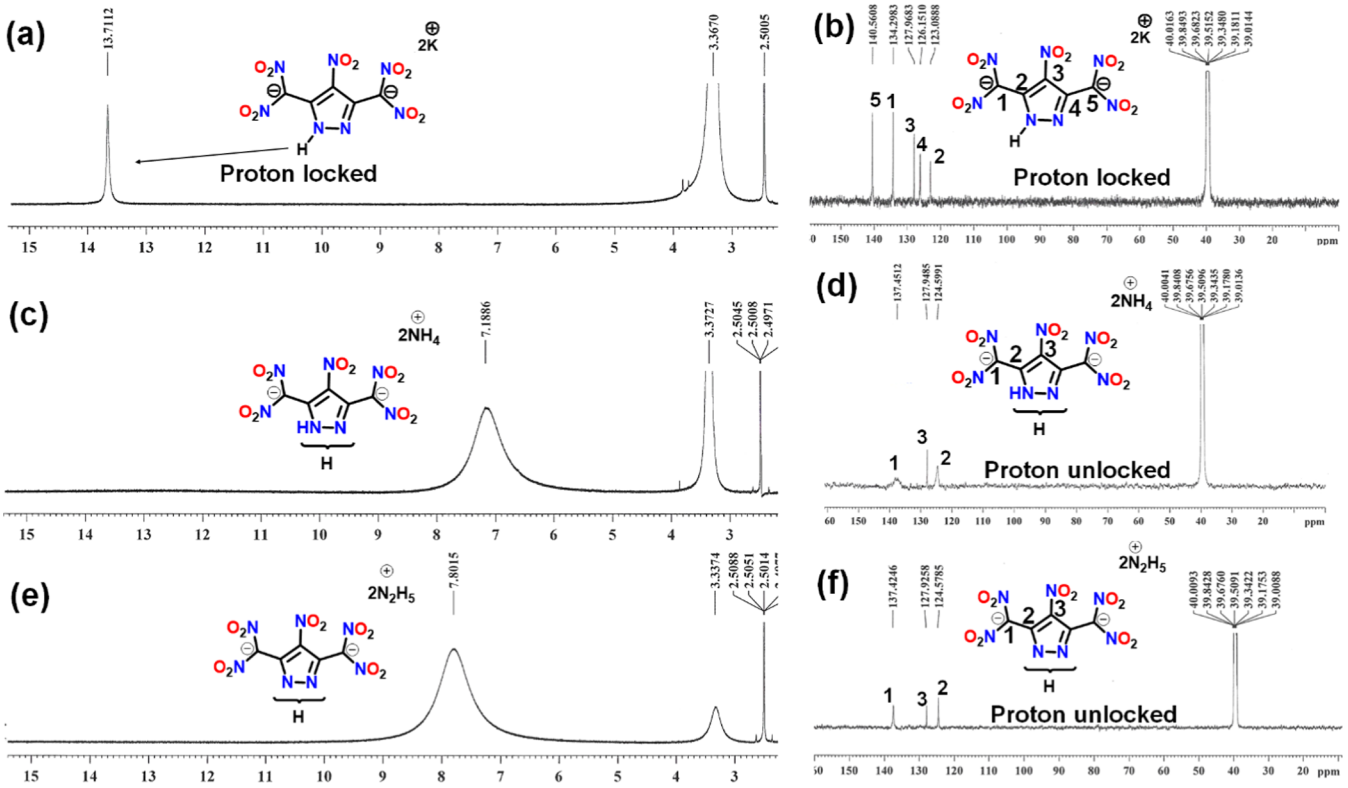

Figure 6. (a, b) ^{1}H and ^{13}C NMRs of compound **5** in dimethyl sulfoxide (DMSO)-d_6. (c, d) ^{1}H and ^{13}C NMRs of compound **6** in DMSO-d_6. (e, f) ^{1}H and ^{13}C NMRs of compound **7** in DMSO-d_6.

Table 1. Compounds 5−7: Energetic Properties

	T_d[a] (°C)	ρ[b] (g cm^{-3})	ΔH_f[c] (kJ mol^{-1})/(kJ g^{-1})	P[d] (GPa)	D_v[e] (m s^{-1})	IS[f] (J)	FS[g] (N)
5	202	2.10	−475.0/−1.19	29.3	7965	6	40
6	176	1.85	−217.3/−0.61	34.5	8688	10	120
7	218	1.83	113.8/0.29	35.9	8931	8	120
i[h]	218	2.13	−421.0/−1.13	27.3	7759	0.1−1	5
ii[i]	190	1.84	10.2/0.03	36.3	8900	19	80
iii[j]	102	1.92	29.4/0.08	29.2	8229	4	240
RDX[k]	204	1.80	92.6/0.42	34.9	8795	7.5	120

[a]Onset decomposition temperature. [b]Measured density (25 °C—gas pycnometer). [c]Calculated molar enthalpy of formation determined using EXPLO5 (version 6.01). [d]Detonation pressure (calculated). [e]Detonation velocity (calculated). [f]Sensitivity—impact (IS). [g]Sensitivity—friction (FS). [h]Ref 5. [i]Ref 6. [j]Ref 7. [k]Ref 38.

The physical properties of energetic compounds, such as sensitivity to impact and sensitivity to friction, are influenced by their crystal packing. Therefore, the Hirshfeld surface analysis and the associated 2D fingerprint plots[39,40] were employed using Crystalexplorer17.5 to understand the role of intermolecular interactions on the properties of compounds **5** and **7** (Figure 7). Strong intermolecular (O···O) interactions arising from oxygen atoms in the nitro groups present in **5** led to high density and more sensitivity to external stimuli (Figure 7c). Compound **7** has lower ratios of O···O interactions (12.4%) in comparison to that of compound **5** (27.8%). Compound **7** also exhibits higher ratios of stabilizing interactions such as O···H and N···H. The hydrogen bonding in **7** plays a major role with 65.7% of the total weak interactions, which decreases the mechanical sensitivity (Figure 7d). The remarkably abundant hydrogen bonds in **7** give rise to low sensitivity and better molecular stability. The calculated results are in excellent agreement with the sensitivity data from the BAM experiments.

CONCLUSIONS

In summary, the challenging syntheses of new compounds containing five nitro groups on a pyrazole ring were achieved. Dipotassium 3,5-bis(dinitromethyl)-4-nitro-1*H*-pyrazole (**5**) was obtained in four steps from the dinitrile derivative **1**. It exhibits a 3D EMOF structure with good thermal stability (202 °C), a high density of 2.15 g cm^{-3} at 100 K (2.10 g cm^{-3} at 298 K), and superior detonation performance (D_v = 7965 m s^{-1}, P = 29.3 GPa). Dihydrazinium 3,5-bis(dinitromethyl)-4-nitro-1*H*-pyrazole (**7**) has a relatively high thermal stability (218 °C) and a density of 1.88 g cm^{-3} at 100 K (1.83 g cm^{-3} at 298 K) arising from the presence of stabilizing 3D hydrogen bonding. Due to their high densities, acceptable thermal stabilities, and good detonation performance, compounds **5**−**7** are attractive as new HEDMs.

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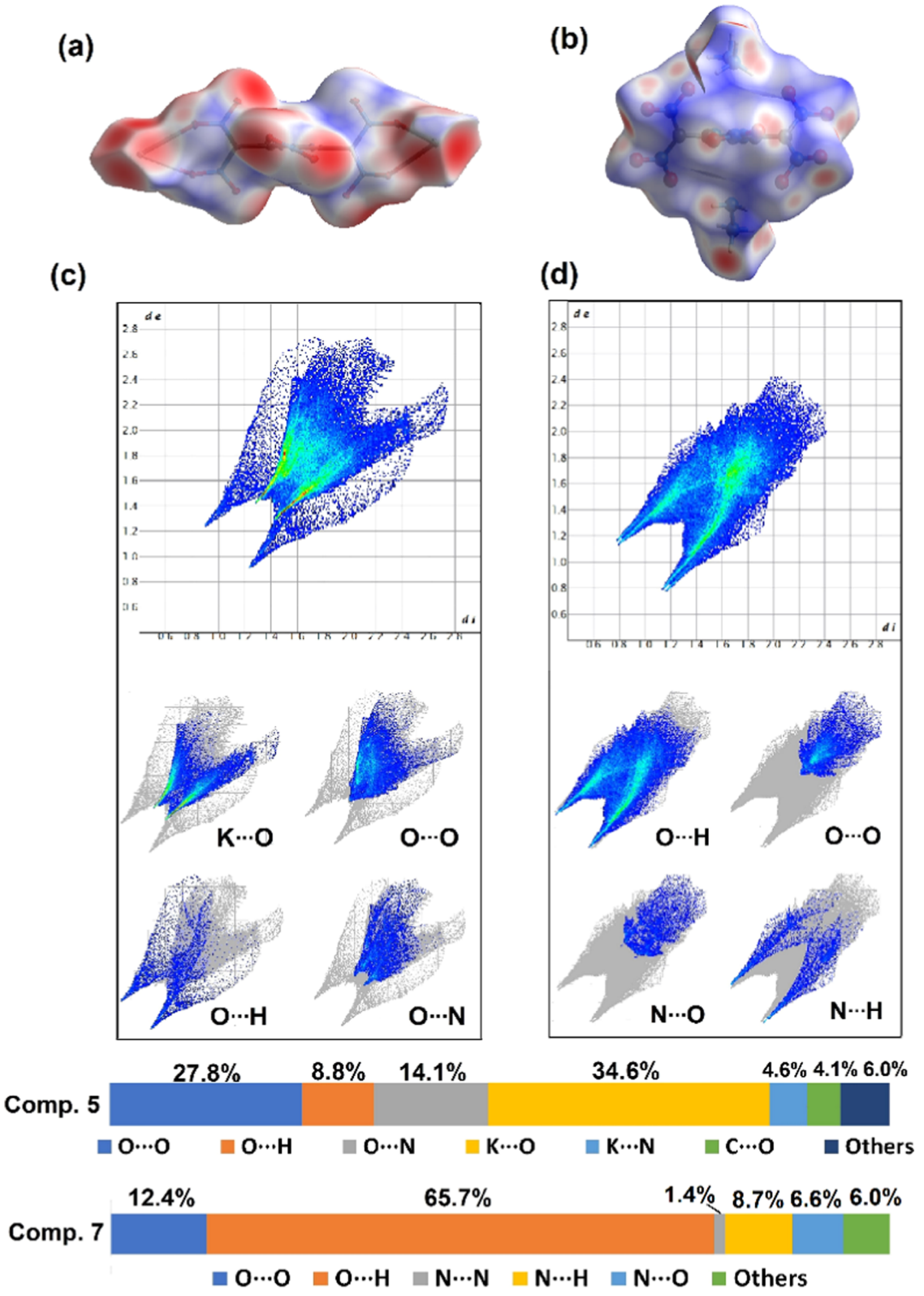

Figure 7. Hirshfeld surface graphs and 2D fingerprint plots of **5** (a, c) and **7** (b, d).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c21510.

Isodesmic reactions, syntheses of **2**–**7**, DSC analysis, ^{1}H, ^{13}C, and ^{14}N NMR data, and X-ray crystal structure parameters of **5** and **7** (PDF)

Crystallographic data for **5** (CIF)

Crystallographic data for **7** (CIF)

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Notes

The authors declare no competing financial interest.

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