

# Synthesis and Properties of 3,6-Dinitropyrazolo[4,3-c]-pyrazole (DNPP) Derivatives

Wenquan Zhang,<sup>[a]</sup> Honglei Xia,<sup>[a]</sup> Rujing Yu,<sup>[b]</sup> Jiaheng Zhang,<sup>\*,[c]</sup> Kangcai Wang,<sup>[a]</sup> and Qinghua Zhang<sup>\*,[a]</sup>

**Abstract:** A series of novel fused-ring pyrazolo[4,3-c]pyrazole derivatives featuring N-dinitromethyl and N-fluorodinitromethyl energetic groups (compounds 3–7) were synthesized using a nine-step reaction. All these compounds were characterized using multinuclear nuclear magnetic resonance (NMR) spectroscopy, infra-red (IR) spectroscopy, and elemental analysis. X-ray diffraction analysis was performed, and the single-crystal structures of compounds 3, 4, 6, and 7 were obtained. For these newly prepared energetic materials, the thermal stability was determined using differential scanning calorimetry (DSC), while the sensitivities were evaluated using BAM drop hammer and friction test. The calculated heat of formation values and the measured densities were used to determine

the detonation parameters, including detonation velocity and pressure, using the EXPLO5 program. Of all the prepared compounds, dipotassium 1,4-bis(dinitromethyl)-3,6-dinitro-1,4-dihydropyrazolo[4,3-c]pyrazole (3) was crystallized as a three-dimensional energetic metal-organic framework (MOF) and showed outstanding detonation performances, which even outperformed the traditional primary explosive lead azide. Compound 7 exhibited a high crystal density of 1.939 g cm<sup>-3</sup>, the high decomposition temperature of 213 °C and desirable impact and friction sensitivities (IS: 12 J; FS: 240 N). These combined properties and performances make these novel fused-ring energetic compounds suitable candidates for high-performance energetic materials.

**Keywords:** energetic materials · high explosive · 3,6-dinitropyrazolo[4,3-c]-pyrazole · fused-ring

## 1 Introduction

Energetic materials that store large amounts of chemical energy are widely used for military and space applications [1–4]. In the past few decades, there has been a growing interest in developing novel nitrogen- and oxygen-rich energetic materials [5–12]. Compared to open-chain or coupled-ring backbones, energetic compounds based on fused-ring moieties have attracted greater attention [13–16]. From the structural point of view, the  $\pi$ -conjugated system is the key factor in improving the solid-state packing coefficient and the density, which are demonstrated in classic energetic compounds, such as furazano-1,2,3,4-tetrazine-1,3-dioxide (FTDO) [17] and 3,6-dinitropyrazolo[4,3-c]pyrazole (DNPP) [18]. In addition to enhanced material density, the rigid structure of fused-ring system and ring strain energy also provide desired intrinsic properties, including heat of formation, detonation velocity and specific energy for both targeting the energetic materials and ensuring molecular stability [19–20]. In pursuit of high-performance energetic materials, the N-functionalization strategies employed in the development of novel fused-ring energetic compounds are intriguing. Recently, several research groups have synthesized various fused-ring-based energetic materials, which exhibit favorable detonation properties (see Scheme 1) [21].


Introducing the *gem*-dinitromethyl explosive group into the molecular scaffold is an efficient way of constructing

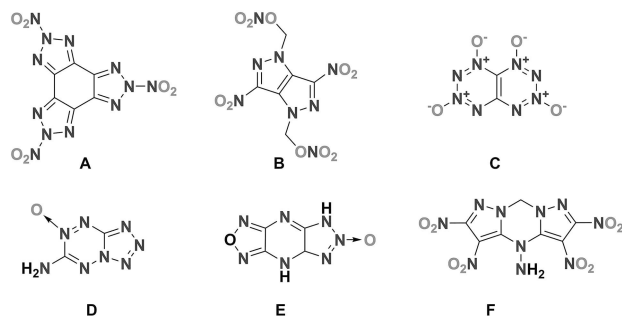
new energetic materials [22]. Molecules containing the *gem*-dinitromethyl fragment usually possess a high nitrogen content and a positive oxygen balance, which ensure their superior detonation performances [23]. Additionally, in contrast to trinitromethyl-containing explosives, the planar structure of a *gem*-dinitromethyl group can provide further stabilization for the whole molecule [24]. The general strategy for the development of *gem*-dinitromethyl-containing energetic materials involves nitration on C-carbonyl structure [25]. Recently, several *gem*-dinitromethyl functionalized energetic compounds, which were based on azole back-

[a] W. Zhang, H. Xia, K. Wang, Q. Zhang  
Institute of Chemical Materials  
China Academy of Engineering Physics (CAEP)  
Mianyang, 621900, China  
\*e-mail: qinghuazhang@caep.cn

[b] R. Yu  
Sichuan Co-Innovation Center for New Energetic Materials  
Southwest University of Science and Technology  
Mianyang, 621900, China

[c] J. Zhang  
School of Materials Science and Engineering  
Harbin Institute of Technology  
Shenzhen, 518055, China  
\*e-mail: zhangjiaheng@hit.edu.cn

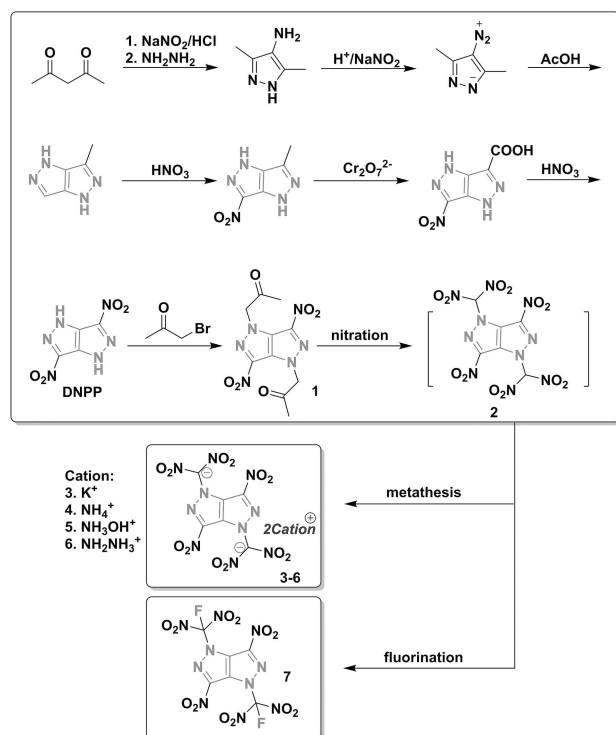
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**Scheme 1.** Several nitrogen-rich fused-ring energetic materials [21].

bones, were developed and showed promising properties for various applications [26].

Based on continuing research interest in fused-ring energetic materials, a new series of *gem*-dinitromethyl functionalized 3,6-dinitropyrazolo[4,3-*c*]-pyrazole derivatives were synthesized using a N-functionalization strategy, followed by subsequent nitration (see Scheme 2). The newly prepared energetic molecules were characterized using X-ray diffraction (XRD), nuclear magnetic resonance (NMR) spectroscopy, infra-red (IR) spectroscopy, thermal stability analysis, and elemental analysis. The energetic properties of these newly prepared compounds were evaluated based on their densities and heat of formations. Some of the pre-



**Scheme 2.** Synthesis of novel pyrazolo[4,3-*c*]pyrazole derivatives featuring the *gem*-dinitromethyl and fluorodinitromethyl functional groups (compounds 3–7).

pared compounds exhibited superior detonation performances than those of traditional highly energetic benchmarks, such as pentaerythritol tetranitrate (PETN) and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX).

## 2 Experimental Section

### 2.1 Safety Precautions

These energetic materials pose a high risk of explosion, and therefore, should be handled with extreme caution to ensure that the experiments are performed safely.

### 2.2 Chemicals

All the organic solvents used were analytical grade and were used as received without further purification. Select-fluor, and bromopropanone were purchased from J&K.

### 2.3 Instrumentation and Analytical Methods

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 600 AVANCE spectrometer (600 and 151 MHz, respectively). High-resolution mass spectrometry was performed on a Shimadzu LCMS-IT-TOF mass spectrometer using electrospray ionization (ESI). Elemental analysis was performed on a Vario MICRO cube elemental analyzer. Thermal properties were measured using TGA/DSC1 and DSC3 Mettler Toledo calorimeter equipped with an auto-cool accessory. Densities were measured on a Micromeritics Accupyc II 1340 gas pycnometer at 25 °C. Single crystal X-ray diffraction data were collected using an Oxford Xcalibur 3 diffractometer with Mo- $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at room temperature. Detonation velocity and detonation pressure data were calculated using the software package EXPLO5 (version 6.02).

### 2.4 Synthesis and Characterization of Energetic Materials

The nitrogen-rich fused-ring precursor, 3,6-dinitropyrazolo[4,3-*c*]pyrazole (DNPP), was synthesized according to previously reported methods [21b.] At first, 1,1'-(3,6-dinitro-3a,6a-dihydropyrazolo[4,3-*c*]pyrazole-1,4-diyl)bis(propan-2-one) (1) was synthesized through the reaction of DNPP and bromopropanone under basic conditions at 70 °C. Then, 1 was treated with concentrated sulfuric acid and 50% nitric acid. After extraction using ethyl acetate, the crude product (2) was obtained and directly used in subsequent synthesis steps. However, pure compound 2 was not obtained using recrystallization or column chromatography due to its molecular instability. In order to stabilize the neutral *gem*-dinitromethyl compound 2, the aqueous/ethyl ether solution of 2 was treated with different bases to obtain ionic

derivatives (compounds 3–6). The fluorodinitromethyl energetic group is another important building block for highly dense energetic materials. Due to the presence of fluorine, energetic materials containing this functional group usually possess high densities and good thermal and molecular stabilities. However, the fluorodinitromethylated compound 7 also exhibits lower heat of formation and oxygen balance than its *gem*-dinitromethyl-containing analogs [22a]. In the current work, 1,4-bis(fluorodinitromethyl)-3,6-dinitro-1,4-dihydropyrazolo[4,3-*c*]pyrazole (7) was synthesized by treating 3 with selectfluor at 25 °C for 1 day. After the addition of dichloromethane and filtration, pure 7 can be obtained by recrystallization with acetonitrile.

**3,6-Dinitropyrazolo[4,3-*c*]pyrazole (DNPP):** DNPP was prepared according to the procedure reported in the literature [21b].

**1,1'-(3,6-dinitro-3a,6a-dihydropyrazolo[4,3-*c*]pyrazole-1,4-diyl)bis(propan-2-one) (1):** DNPP (8.00 g, 40 mmol) was added to a solution of potassium hydroxide (4.49 g, 80 mmol), water (30 mL) and acetone (30 mL). Then, bromopropanone (7.06 mL, 84 mmol) was added to the resulting solution. After stirring at 70 °C for 8 hours, the yellow precipitate was filtered, washed with 30 mL water and 30 mL hot methanol, and then dried in air to obtain 1 as a pale-yellow solid with high yield (86%).

**Dipotassium 1,4-bis(dinitromethyl)-3,6-dinitro-1,4-dihydropyrazolo[4,3-*c*]pyrazole (3):** Compound 1 (1.86 g, 6 mmol) was added in portions to a mixture of concentrated sulfuric acid (25 mL) at 5 °C. And then, 50% nitric acid (4 mL) was added to the mixture, and the mixture was stirred at 40 °C for 1 hour, cooled to 20 °C, and kept at this temperature for 1 hour. The mixture was poured into ice and extracted using ethyl acetate. The organic layer was washed thrice with a small amount of water and then dried using anhydrous sodium sulphate. After removing the solvent, the crude product of 2 was obtained as dark yellow solid (Pure compound 2 cannot be purified from the crude product, perhaps due to its poor stability). The crude product was dissolved in a small amount of water, and potassium bicarbonate (1.2 g, 12 mmol) was added. The precipitate was filtered, washed thrice with methanol (3 × 5 mL), and then dried in air to obtain 3 as a yellow solid with 45% yield. <sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>): δ 138.76, 132.52; IR (KBr, cm<sup>-1</sup>): 1563, 1494, 1385, 1248, 1153, 1033, 853, 818; HRMS (ESI) *m/z* anion calculated for C<sub>6</sub>HN<sub>10</sub>O<sub>12</sub> [M]<sup>-</sup>: 404.9781, found: 404.9763; elemental analysis calculated (%) for C<sub>6</sub>K<sub>2</sub>N<sub>10</sub>O<sub>12</sub>: C 14.94, N 29.04, found: C 14.63, N 28.89.

**Synthesis of compounds 4–6:** Compound 3 was acidified with dilute sulfuric acid and extracted with ethyl ether. Either a solution of ammonia in methanol, 50% hydroxylamine in water, or a solution of 80% hydrazine hydrate was added to a solution of 2 in ethyl ether, respectively. After stirring at room temperature for 1 hour, the precipitate was filtered and washed with a small amount of methanol to obtain compounds 4–6, respectively.

**Diammonium 1,4-bis(dinitromethyl)-3,6-dinitro-1,4-dihydropyrazolo[4,3-*c*]pyrazole (4):** Yield: 95%, yellow solid. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): δ 7.07 (s, 8H, NH<sub>4</sub>); <sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>): δ 138.76, 132.52; IR (KBr, cm<sup>-1</sup>): 1564, 1501, 1437, 1413, 1386, 1277, 1246, 1216, 1165, 1036, 857, 820; HRMS (ESI) *m/z* anion calculated for C<sub>6</sub>HN<sub>10</sub>O<sub>12</sub>[M]<sup>-</sup>: 404.9781, found: 404.9763; elemental analysis calculated (%) for C<sub>6</sub>H<sub>8</sub>N<sub>12</sub>O<sub>12</sub>: C 16.37, H 1.83, N 38.18, found: C 16.21, H 1.90, N 38.03.

**Dihydroxylammonium 1,4-bis(dinitromethyl)-3,6-dinitro-1,4-dihydropyrazolo[4,3-*c*]pyrazole (5):** Yield: 96%, yellow solid. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): δ 8.16 (s, 8H, NH<sub>3</sub>-OH); <sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>): δ 138.76, 132.52; IR (KBr, cm<sup>-1</sup>): 1554, 1494, 1393, 1200, 1148, 1128, 1031, 856, 819; C<sub>6</sub>HN<sub>10</sub>O<sub>12</sub> [M]<sup>-</sup>: 404.9781, found: 404.9763; elemental analysis calculated (%) for C<sub>6</sub>H<sub>8</sub>N<sub>12</sub>O<sub>14</sub>: C 15.26, H 1.71, N 35.60, found: C 15.06, H 1.82, N 35.06.

**Dihydrazinium 1,4-bis(dinitromethyl)-3,6-dinitro-1,4-dihydropyrazolo[4,3-*c*]pyrazole (6):** Yield: 94%, yellow solid. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): δ 6.86 (s, 10H, NH<sub>2</sub>-NH<sub>3</sub>); <sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>): δ 138.78, 132.53; IR (KBr, cm<sup>-1</sup>): 1562, 1500, 1387, 1271, 1209, 1033, 855, 819; HRMS (ESI) *m/z* anion calculated for C<sub>6</sub>HN<sub>10</sub>O<sub>12</sub>[M]<sup>-</sup>: 404.9781, found: 404.9763; elemental analysis calculated (%) for C<sub>6</sub>H<sub>10</sub>N<sub>14</sub>O<sub>12</sub>: C 15.33, H 2.14, N 41.70, found: C 15.20, H 2.19, N 41.53.

**1,4-Bis(fluorodinitromethyl)-3,6-dinitro-1,4-dihydropyrazolo[4,3-*c*]pyrazole (7):** Selectfluor (2 mmol) was added to a suspension of 3 (1 mmol) in anhydrous acetonitrile (5 mL). The mixture was stirred at 25 °C for 1 day. Dichloromethane (5 mL) was then added to it. The precipitate was filtered, and the filtrate was concentrated in vacuo, producing 7 as the yellow solid. Compound 7 can be purified using recrystallization from acetonitrile to produce a white crystal (Yield 68%). <sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>): δ 142.65, 132.17, 115.12 (*J*<sub>CF</sub> = 310.2 Hz); IR (KBr, cm<sup>-1</sup>): 1623, 1578, 1373, 1255, 1199, 988, 846, 823, 804; HRMS (ESI) *m/z* cation calculated for C<sub>6</sub>HF<sub>2</sub>N<sub>10</sub>O<sub>12</sub> [M-H]<sup>+</sup>: 442.9743, found: 442.9732; elemental analysis calculated (%) for C<sub>6</sub>F<sub>2</sub>N<sub>10</sub>O<sub>12</sub>: C 16.30, N 31.68, found: C 16.25, N 31.62.

## 3 Results and Discussion

### 3.1 Structural Characterization

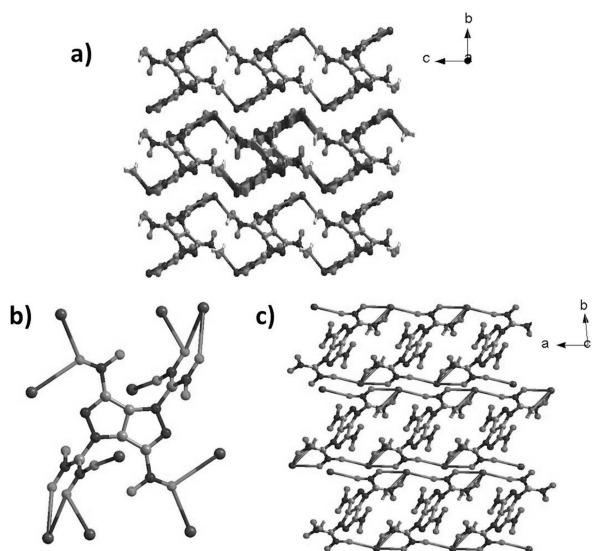
In the <sup>1</sup>H NMR spectra, there were no hydrogen signals corresponding to either 1,4-bis(dinitromethyl)-3,6-dinitro-1,4-dihydropyrazolo [4,3-*c*]pyrazole anion or 1,4-bis(fluorodinitromethyl)-3,6-dinitro-1,4-dihydropyrazolo[4,3-*c*]pyrazole (7). For compounds 4–6, all the hydrogen signals originated from nitrogen-rich cations. In the <sup>13</sup>C NMR, two signals (δ values of 139 and 133 ppm) were assigned to the fused-ring system, while the C-fluorodinitro signals were observed at around 115 ppm. The vibrational analysis for the newly prepared compounds showed both the characteristic asymmetric -NO<sub>2</sub> stretching vibrations around

1600  $\text{cm}^{-1}$  and the symmetric stretching vibrations around 1200  $\text{cm}^{-1}$ . For X-ray diffraction analysis, suitable crystals of compounds **3**, **4**, **6**, and **7** were obtained through slow recrystallization using methanol at room temperature.

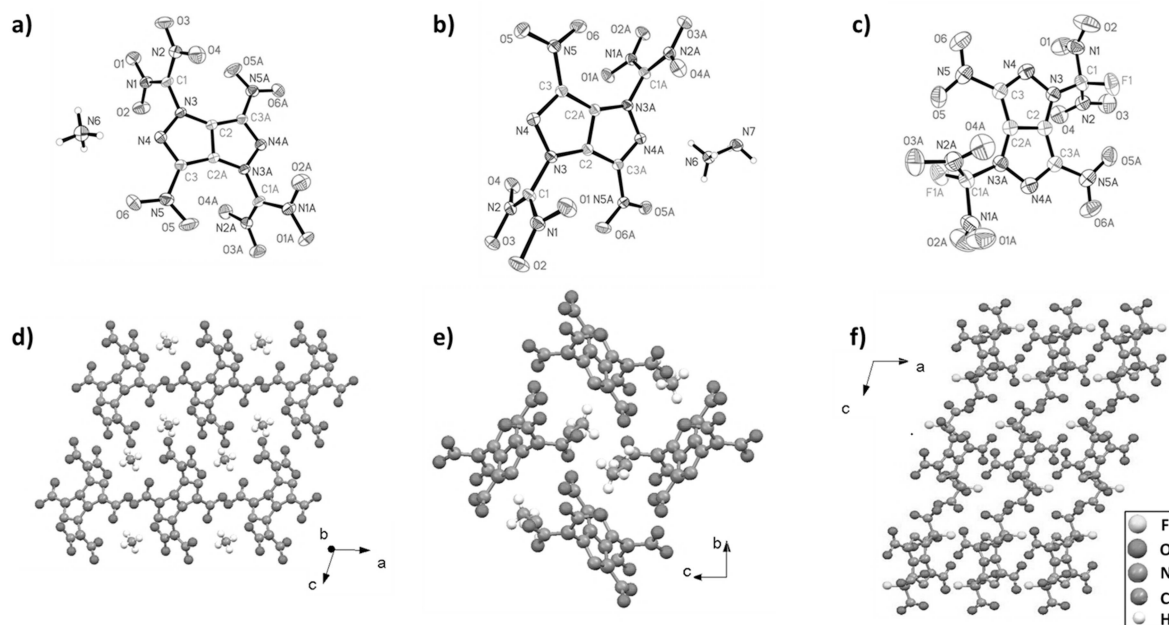
Compound **3** crystallizes in a triclinic (*P*-1) space group, and each unit cell contains four K ions and two pyrazolo[4,3-*c*]pyrazolate anions (Figure 1). The potassium ions act as multi-coordination sites, while the anions act as polydentate ligands, forming a three-dimensional (3D) metal-or-

ganic framework (MOF). The planar structure of the pyrazolo[4,3-*c*]pyrazole and the nitro groups provides the lower energy confirmation for those two moieties by maximizing the delocalization. The dinitromethyl moiety is orthogonal to the ring, due to the steric strain in the system. This packing allows the cations to pack nicely between the molecules. Additionally, potassium ions coordinate to N from pyrazolo[4,3-*c*]pyrazole rings and O from nitro groups. For the anion, the nitro groups are coplanar with the fused-ring due to the coordination interaction of K and O from the *gem*-dinitromethyl group, and the torsion angle of the *gem*-dinitromethyl group and pyrazolo[4,3-*c*]pyrazole ring is about 80°. The bond lengths for K–O range from 2.663 Å to 2.965 Å, whereas the bond length of K–N is 2.979 Å. Because of the rigid fused-ring, many holes exist in the crystal. Two kinds of holes (5.12 Å × 3.58 Å and about 5.10 Å × 8.24 Å) are presented in the 3D framework, resulting in a density of 2.016  $\text{g cm}^{-3}$ .

Compound **4** crystallizes in a monoclinic (*C*12/*c*1) space group with four anions and eight ammonium cations per unit cell (see Figures 2a and 2d). The stacking density of crystal is determined to be 1.784  $\text{g cm}^{-3}$  at room temperature. The anion belongs to centrosymmetric two nitro groups, which are coplanar with the fused-ring system. All the atoms of the *gem*-dinitromethyl group are almost coplanar, and the average torsion angle between the *gem*-dinitromethyl group and pyrazolo[4,3-*c*]pyrazole ring is 73.8°. The bond lengths for C1–N1/2, C1–N3, and C3–N5 are 1.3775/1.3848 Å, 1.3967 Å and 1.4428 Å, respectively, which fall well within the normal range for C–NO<sub>2</sub>. The hydrogen atoms of ammonium and the adjacent oxygen atoms of nitro groups form a number of hydrogen bonds,



**Figure 1.** (a) The 3D MOF of **3** depicted along the crystallographic *a*-axis; (b) Coordination structure of **3**; (c) The 3D MOF of **3** depicted along the crystallographic *c*-axis.



**Figure 2.** (a–c) X-ray crystal structure of **4**, **6** and **7**; (d–f) Packing diagram of **4**, **6** and **7**.

whereas the lengths of N–H...O lie within the range of 2.09–2.21 Å. From the *b*-axis view, the arrangement of the crystal is zigzag. Similar to compound **4**, **6** crystallizes with a monoclinic (*P*121/*n*1) symmetry having two anions and four hydrazinium cations in each unit cell (see Figures 2b and 2e). Compound **6** has a density of 1.813 g cm<sup>−3</sup> at 298 K. The structural characterization for the anion in compound **6** is almost the same as that of **4**, whereas the torsion angle between the *gem*-dinitromethyl group and the pyrazolo[4,3-*c*]pyrazole ring is around 83°. Compound **7** also crystallizes in a monoclinic (*P*121/*c*1) space group with four molecules per unit cell, and the crystal density was found to be 1.939 g cm<sup>−3</sup> at room temperature (see Figures 2c and 2f). Although the molecular configuration changed due to the introduction of fluorine, the entire fused-ring and C3/C3-A-nitro groups were coplanar. The configuration of C1 belonging to the *gem*-dinitromethyl group is almost a regular tetrahedron, while the bond angles for N1–C1–N2 to N2–C1–N3 range from 107.02° to 112.25°. The bond lengths of C1–N1/N2, C1–N3, C3–N5 are 1.5528/1.5479 Å, 1.4204 Å, and 1.4522 Å, respectively. Due to the influence of fluorine, the corresponding C–N bonds are longer than those of **4**.

### 3.2 Properties Evaluation

The thermal stabilities of newly prepared compounds **3–7** were determined using differential scanning calorimetry (DSC) with the heating rate of 5 °C min<sup>−1</sup> (see Table 1). Although the neutral 1,4-bis(dinitromethyl)-3,6-dinitro-1,4-dihydropyrazolo[4,3-*c*]pyrazole (**2**) is not stable at room temperature, its energetic salts have much better thermal stability, resulting in decomposition temperatures ranging from 113 °C (**6**) to 187 °C (**3**). Besides **3**, 1,4-bis(fluorodinitromethyl)-3,6-dinitro-1,4-dihydropyrazolo[4,3-*c*]pyrazole (**7**) also possesses a high decomposition temper-

ature of 213 °C, which supports the higher thermal stability of fluorodinitromethyl group than that of the *gem*-dinitromethyl group.

The densities of newly prepared compounds were measured using a gas pycnometer at room temperature and were verified using the crystal densities. The density values, which range from 1.784 cm<sup>−3</sup> (**4**) to 1.939 g cm<sup>−3</sup> (**7**), which are comparable to that of RDX (1.82 g cm<sup>−3</sup>). The relatively high densities of compounds **3** (2.016 g cm<sup>−3</sup>), **5** (1.855 g cm<sup>−3</sup>), and **7** (1.939 g cm<sup>−3</sup>) presumably result from the metal ion, the oxygen-containing cation, and the fluorodinitromethyl group, respectively. In particular, the significant improvement of density in **7** supports the advantage of introducing fluorodinitromethyl energetic group into nitrogen-rich fused-ring frameworks. In this work, the heats of formation for 1,4-bis(dinitromethyl)-3,6-dinitro-1,4-dihydropyrazolo[4,3-*c*]pyrazolate anion and **7** were obtained using the isodesmic reaction approach. For energetic ionic compounds **4–6**, the solid-state heats of formation were calculated by employing Born-Haber energy cycles, and the values are found to be 188.85 kJ mol<sup>−1</sup>, 288.78 kJ mol<sup>−1</sup> and 497.49 kJ mol<sup>−1</sup>, respectively.

With the obtained values of molecular formulae, measured densities, and heats of formation, the energetic performances for compounds **3–7** were evaluated using the EXPLO5 program. With respect to the detonation velocity (*v*<sub>D</sub>) and detonation pressure (*P*), the values of these newly prepared materials (*v*<sub>D</sub>: 8582–9148 m s<sup>−1</sup>; *P*: 31.74–37.28 GPa) are comparable to the values of PETN (*v*<sub>D</sub>: 8564 m s<sup>−1</sup>; *P*: 31.3 GPa). Of all these compounds, **5** exhibits the best energetic performance and shows superior results than those of the highly explosive RDX (*v*<sub>D</sub>: 8724 m s<sup>−1</sup>; *P*: 35.2 GPa). For initial safety testing, the sensitivities of compounds **3–6** (impact sensitivity: 2–5 J; friction sensitivity: 20–90 N) were all lower than those of the RDX (impact sensitivity: 7.4 J; friction sensitivity: 120 N). However, the sensitivities were close to those of PETN (IS: 3 J; FS: 60 N). There-

**Table 1.** Properties of **3–7** compared with RDX and PETN.

Compound	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	RDX <sup>n</sup>	PETN <sup>o</sup>
Formula <sup>[a]</sup>	C <sub>6</sub> H <sub>4</sub> K <sub>2</sub> N <sub>10</sub> O <sub>14</sub>	C <sub>6</sub> H <sub>8</sub> N <sub>12</sub> O <sub>12</sub>	C <sub>6</sub> H <sub>8</sub> N <sub>12</sub> O <sub>14</sub>	C <sub>6</sub> H <sub>10</sub> N <sub>14</sub> O <sub>12</sub>	C <sub>6</sub> F <sub>2</sub> N <sub>10</sub> O <sub>12</sub>	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>	C <sub>5</sub> H <sub>8</sub> N <sub>4</sub> O <sub>12</sub>
FW [g mol <sup>−1</sup> ] <sup>[b]</sup>	518.35	440.20	472.20	470.23	442.12	222.12	316.14
N [%] <sup>[c]</sup>	27.02	38.18	35.60	41.70	31.68	37.84	17.72
Ω [%] <sup>[d]</sup>	−3.09	−14.54	−6.78	−17.01	3.62	−21.61	−10.12
ρ [g cm <sup>−3</sup> ] <sup>[e]</sup>	2.016	1.784	1.855 <sup>[i]</sup>	1.813	1.939	1.81	1.77
<i>T</i> <sub>dec</sub> [°C] <sup>[f]</sup>	113 <sup>[m]</sup>	169	187	165	213	210	160
IS [J] <sup>[g]</sup>	2	3	2	5	12	7.5	3
FS [N] <sup>[h]</sup>	30	90	20	60	240	120	60
Δ <i>H</i> <sub>f</sub> [kJ mol <sup>−1</sup> ] <sup>[i]</sup>	−527.41	188.85	288.78	497.49	−51.15	86.3	−502.8
<i>v</i> <sub>D</sub> [m s <sup>−1</sup> ] <sup>[j]</sup>	9018	8677	9148	8984	8582	8878	8564
<i>P</i> [GPa] <sup>[k]</sup>	33.63	33.01	37.28	36.12	31.74	34.8	31.3

[a] Molecular formula. All new compounds are anhydrous. [b] Formula weight. [c] Nitrogen content. [d] OB for C<sub>6</sub>H<sub>6</sub>O<sub>6</sub>N<sub>6</sub>, based on CO<sub>2</sub>. [e] Crystal density at room temperature. [f] Decomposition temperature (onset). [g] Impact sensitivity, BAM drop hammer. [h] Friction sensitivity, BAM friction tester. [i] Heat of formation. [j] Detonation velocity (calculated with Explo5 v6.02). [k] Detonation pressure (calculated with Explo5 v6.02). [l] Density measured by gas pycnometer (25 °C). [m] The salt **3** loss water at 113 °C and decomposed at 215 °C. [n] Ref. [16]. [o] Ref. [27].

fore, these ionic derivatives are highly sensitive to impact and friction. Nevertheless, they still exhibit good densities and thermal stabilities, which can enable them to be used as potential primary explosives. Notably, the neutral **7** affords a surprisingly high density of  $1.939\text{ g cm}^{-3}$ , and its calculated detonation velocity and pressure are up to  $8582\text{ m s}^{-1}$  and  $31.74\text{ GPa}$ , respectively. Obviously, as compared to *gem*-dinitromethyl-containing analogs, **7** possesses relatively lower mechanical sensitivities towards impact and friction (impact sensitivity:  $12\text{ J}$ ; friction sensitivity:  $240\text{ N}$ ) and higher crystal density, which demonstrates its potential application as a promising secondary explosive. The crystal packing can be effectively reflected by Hirshfeld surfaces. In this work, the 2D-fingerprint plots of crystals and the associated Hirshfeld surfaces of compounds **4** and **6** were employed to study the intermolecular interactions. As shown in Figures 3a and 3d, the fused-rings show planar structure and appear plate-shaped. However, the torsion angle between the *gem*-dinitromethyl group and the pyrazolo[4,3-*c*]pyrazole ring can be found. The red and blue in Hirshfeld surfaces denote the high and low close contact populations, respectively. The red dots mainly denote the intermolecular H $\cdots$ O and O $\cdots$ H interactions. This can be ascertained by the two-dimensional fingerprint plots shown in Figures 3b and 3e. A pair of remarkable spikes in the bottom-left of the 2D fingerprint plots of the crystal denote hydrogen bonds among neighboring intralayer molecules. Additionally,

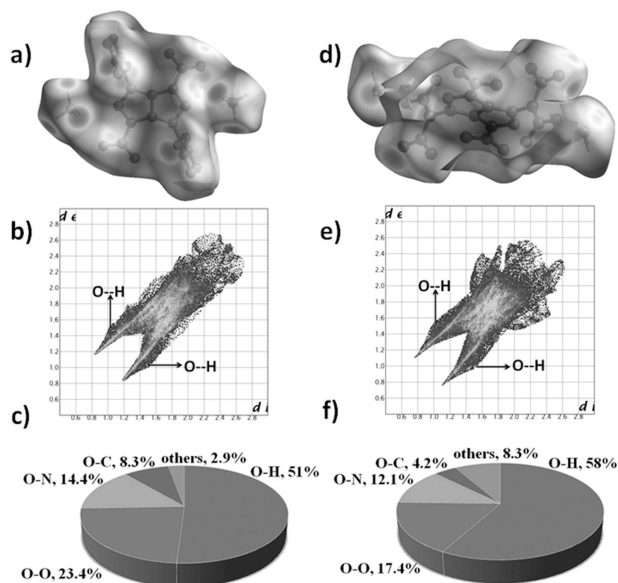
hydrogen bonding interaction is an important characteristic of ionic salts and is able to reflect the sensitivity. Usually, large amounts of hydrogen bonds in crystal packing are beneficial to lower sensitivity of ionic salts. From the atomic contacts percentage shown in Figures 3c and 3f, the O $\cdots$ H possess 51% and 58% of the total weak interactions for compounds **4** and **6**, respectively, which means that the hydrogen bonds can provide more stabilization for Compound **6**. And this is again in agreement with the experimental IS and FS values, where compound **6** is found to be more stable than compound **4**.

## 4 Conclusion

In this work, five fused-ring energetic derivatives of 3,6-dinitropyrazolo[4,3-*c*]pyrazole (compounds **3**–**7**), including four *gem*-dinitromethyl functionalized ionic compounds and one fluorodinitromethyl-containing analog were synthesized. The synthesized derivatives were characterized using various spectroscopy techniques. The structures of compounds **3**, **4**, **6** and **7** were confirmed using single-crystal X-ray diffraction analysis. The energetic performances were theoretically evaluated using both Gaussian 03 and EXPLO 5 programs. The results indicate that these compounds have the potential to compete with traditional primary explosive PETN, and in some cases, approach the performance of typical high explosive RDX. Among these newly prepared compounds, highly energetic dipotassium salt of 1,4-bis(dinitromethyl)-3,6-dinitro-1,4-dihydropyrazolo[4,3-*c*]pyrazole (**3**) was crystallized as an interesting three-dimensional metal-organic framework and showed outstanding detonation performances, which are comparable to that of the traditional primary explosive lead azide. The fluorodinitromethyl-containing **7** can be used as a second explosive and affords a high crystal density of  $1.939\text{ g cm}^{-3}$ , high thermal decomposition temperature of  $213^\circ\text{C}$  and desired mechanical sensitivities towards non-explosive stimuli (impact sensitivity:  $12\text{ J}$ ; friction sensitivity:  $240\text{ N}$ ). Therefore, **7** demonstrates its promise as a potential replacement for the commonly used explosive, RDX. Additionally, the newfound *gem*-dinitromethyl- or fluorodinitromethyl-containing energetic compounds further enrich the energetic compound library of pyrazolo[4,3-*c*]pyrazoles and broaden the options for the design of novel fused-ring energetic materials.

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**Figure 3.** Hirshfeld surface calculations for **4** (a–c) and **6** (d–f). Images (a) and (d) show the Hirshfeld surfaces for compounds **4** and **6** (white, distance  $d$  equals the van der Waals distance; blue,  $d$  exceeds the van der Waals distance; red,  $d$  is less than the van der Waals distance). Images (b) and (e) show the two-dimensional fingerprint plots in crystals for compounds **4** and **6**. Images (c) and (f) show the individual atomic contacts percentage contribution to Hirshfeld surfaces for compounds **4** and **6**, respectively.



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