

## PAPER

[View Article Online](#)  
[View Journal](#) | [View Issue](#)Cite this: *Dalton Trans.*, 2024, **53**, 4035

# Obtaining superior high-density fused-ring energetic materials *via* the introduction of carbonyl, *o*-NH<sub>2</sub>–NO<sub>2</sub> and nitroamino groups†

Xiaoyu Guo,<sup>‡a</sup> Yizhen Feng,<sup>‡a</sup> Shengjie Zhi,<sup>a</sup> Yajie Fu,<sup>a</sup> Yingle Liu,<sup>id</sup> <sup>\*a,c</sup>  
Qiangqiang Liu<sup>a</sup> and Haixiang Gao<sup>id</sup> <sup>\*b</sup>

Two carbonyl and *o*-NH<sub>2</sub>–NO<sub>2</sub>-containing energetic materials and their analogues were effectively designed, synthesized and fully characterized with multinuclear NMR, IR and elemental analyses. Their structures were also further confirmed *via* X-ray diffraction. Among them, compound **7** exhibits good potential for application as a secondary explosive with extremely high density (2.04 g cm<sup>−3</sup>), good sensitivity (IS > 40 J, FS > 360 N), and excellent calculated detonation performance ( $D_v = 8943 \text{ m s}^{-1}$ ,  $P = 35.0 \text{ GPa}$ ). Furthermore, a detailed comparative study based on X-ray diffraction, Hirshfeld surfaces and 2D fingerprint plots among compounds **4**, **7** and **9** has demonstrated that the density and detonation performance could be effectively improved *via* introducing a carbonyl group into fused-ring compounds. More importantly, the sensitivity of the resulting energetic materials did not deteriorate. Obviously, this strategy *via* introducing carbonyl, *o*-NH<sub>2</sub>–NO<sub>2</sub> and nitroamino groups into fused-ring energetic compounds will help in the design of next-generation high-energy and insensitive fused-ring energetic materials.

Received 18th December 2023,  
Accepted 26th January 2024

DOI: 10.1039/d3dt04237e

[rsc.li/dalton](https://rsc.li/dalton)

## 1. Introduction

As an important component of explosives, propellants, pyrotechnic agents, *etc.*, energetic materials have attracted considerable attention.<sup>1,2</sup> Compared with traditional energetic materials, which mainly produce carbon monoxide or carbon dioxide after combustion, nitrogen-rich high energy density materials (HEDMs) are friendlier to the environment because nitrogen is almost the only explosive product.<sup>3</sup> In the past decades, a great number of nitrogen-rich energetic materials with excellent detonation performance have been created.<sup>4</sup> However, most of them fail to meet the requirements of practical applications due to the contradictory relationship between energy and safety.<sup>5</sup> Considering that accidents are likely to occur during the preparation, storage, transportation, and application of sensitive explosives, designing and synthesizing

insensitive high energy density materials has become particularly important.

Hydrogen bonding is a strong guiding force that could reduce the localized heating of energetic materials from external stimuli.<sup>6</sup> Therefore, the formation of extended hydrogen bonding *via* molecular structure design has become an important strategy to create insensitive energetic materials.<sup>7</sup> Among them, *o*-nitro-amino and *o*-*N*-oxide-amino tend to form intramolecular hydrogen bonding that can easily increase the coplanarity of molecular structures and form good crystal stacking.<sup>8</sup> As a result, this class of energetic materials usually has high density and stability. Typical representatives (Fig. 1), such as 2,4,6-triamino-1,3,5-trinitrobenzene (**I**),<sup>9</sup> 3,8-dinitropyrazolo[5,1-*c*][1,2,4]triazine-4,7-diamine (**II**),<sup>10</sup> 2,4,6-triamino-5-nitropyrimidine-1,3-dioxide (**III**)<sup>11</sup> and 3,6-diamino-1,2,4-triazolo[4,3-*b*][1,2,4,5]tetrazine-7-*N*-oxide (**IV**),<sup>12</sup> possess exceptionally high density ( $\rho > 1.82 \text{ g cm}^{-3}$ ), good thermal stability ( $T_d > 196 \text{ }^\circ\text{C}$ ), excellent insensitivity (IS > 40 J, FS > 360 N) and excellent detonation performance ( $D_v > 8540 \text{ m s}^{-1}$ ,  $P > 32.1 \text{ GPa}$ ). The formation of intermolecular hydrogen bonding is influenced by the molecular structure and the method of crystal stacking.<sup>13</sup> At present, researchers mainly use Hirshfeld surfaces and 2D fingerprint plots to explore the types and proportions of intermolecular hydrogen bonding.<sup>14</sup>

Density is an important parameter in determining the detonation performance of energetic materials. Generally, the introduction of traditional energetic groups, such as –NO<sub>2</sub>,

<sup>a</sup>Key Laboratory of Green Catalysis of Higher Education Institutes of Sichuan, College of Chemistry and Environmental Engineering, Sichuan University of Science and Engineering, Zigong 643000, China. E-mail: [liuyingleyou@163.com](mailto:liuyingleyou@163.com)

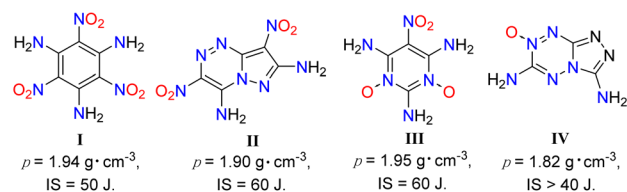
<sup>b</sup>Department of Applied Chemistry, China Agricultural University, Beijing 100193, China. E-mail: [hxgao@cau.edu.cn](mailto:hxgao@cau.edu.cn)

<sup>c</sup>Beijing Institute of Technology Chongqing Innovation Center, Chongqing 401120, China

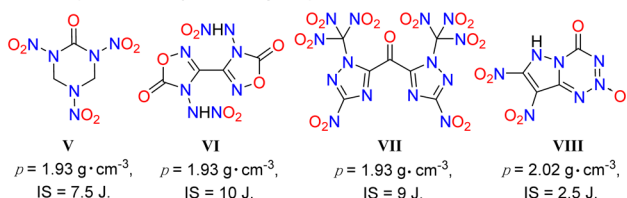
† Electronic supplementary information (ESI) available. CCDC 2306222–2306224. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3dt04237e>

‡ These authors contributed equally to this work.

## (a) Examples of hydrogen bonding compounds.



## (b) Examples of carbonyl-containing compounds.



## (c) Example of this work.

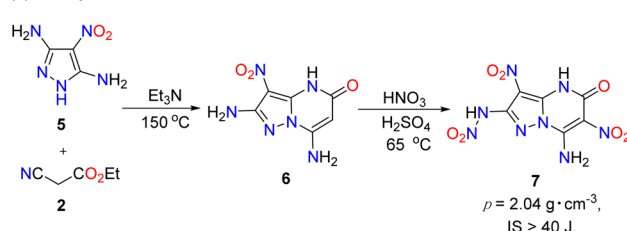


Fig. 1 Energetic materials studied previously and in this work.

–NHNO<sub>2</sub>, –CH(NO<sub>2</sub>)<sub>2</sub> and –C(NO<sub>2</sub>)<sub>3</sub>, can improve the density of precursor compounds. However, these groups also increase the sensitivity concomitantly.<sup>15</sup> Recently, the carbonyl group (C=O) has been attracting a lot of attention from numerous researchers because it can significantly increase density without a concomitant deterioration in the sensitivity of energetic materials.<sup>16</sup> For example, 1,3,5-trinitro-1,3,5-triazinane (**V**) has a higher density (1.93 g cm<sup>–3</sup>)<sup>17</sup> and close impact sensitivity (IS = 7.5 J) compared to those of cyclotrimethylenetrinitramine (**RDX**) ( $\rho = 1.81 \text{ g cm}^{-3}$ , IS = 7.4 J). Other compounds containing carbonyl groups, such as 3-nitro-1,2,4-triazol-5-one (**NTO**),<sup>18</sup> *N,N'*-(5,5'-dioxo-[3,3'-bi(1,2,4-oxadiazole)]4,4'-(5*H*,5'*H*)-diyl)dinitramide (**VI**),<sup>19</sup> bis(3-nitro-1-(trinitromethyl)-1*H*-1,2,4-triazol-5-yl)-methanone (**VII**)<sup>20</sup> and 7,8-dinitro-4-oxo-4,6-dihydropyrazolo[5,1-*d*][1,2,3,5]tetrazine 2-oxide (**VIII**),<sup>21</sup> have excellent density (up to 2.02 g cm<sup>–3</sup>). Upon careful analysis of the synthetic routes of these compounds, it is easily found that the carbonyl groups in these compounds were introduced through the use of strong oxidants or toxic reagents, which limited the large-scale preparation of these compounds. More importantly, these compounds are generally sensitive (IS < 10 J). Therefore, it is necessary to develop new methods for preparing insensitive carbonyl-containing fused-ring energetic materials.

Enaminone, having a nucleophilic enamine and an electrophilic ketone structure, is an extremely popular backbone in the synthesis of fused-ring compounds.<sup>22</sup> Recently, 7-amino-pyrazolo[1,5-*a*]pyrimidin-5(4*H*)-one was synthesized by some pharmaceutical chemists *via* the reaction of ethyl cyanoacetate with 5-aminopyrazole compounds.<sup>23</sup> Considering the high nucleophilicity of the carbon atom between the amino group and carbonyl, a nitro group can be easily introduced by a

nitration reaction;<sup>24</sup> herein, we report a method for the synthesis of pyrazolo[1,5-*a*]pyrimidin-5(4*H*)-one energetic compounds **4** and **7**, which possess carbonyl and *o*-NH<sub>2</sub>–NO<sub>2</sub> groups. Among them, compound **7** exhibits extremely high density (2.04 g cm<sup>–3</sup>), excellent sensitivity (IS > 40 J, FS > 360 N), and exceptionally high calculated detonation performance ( $D_v = 8943 \text{ m s}^{-1}$ ,  $P = 35.0 \text{ GPa}$ ). A detailed comparative study among compounds **4**, **7** and the analogue **9** based on X-ray diffraction, Hirshfeld surfaces, and 2D fingerprint plots has further demonstrated that the density and detonation performance of the resulting carbonyl-containing fused-ring compounds could be improved significantly without a concomitant deterioration in the sensitivity of energetic materials. Clearly, introducing these groups into fused-ring energetic compounds is a useful method for designing next-generation high-energy and insensitive energetic materials.

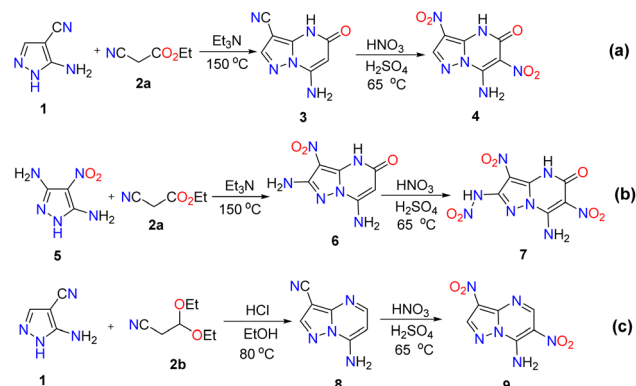
## 2. Results and discussion

### 2.1. Synthesis

As shown in Scheme 1, 7-amino-5-oxo-4,5-dihydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**3**) was smoothly synthesized in 78% yield *via* a reflux reaction of known compound **1** and ethyl 2-cyanoacetate (**2a**) in the presence of triethylamine (Scheme 1, eqn (a)). Then, the cyano and the carbon atom between the amino group and the carbonyl group of compound **3** were fully substituted with nitro groups using a standard nitration system consisting of a mixture of nitric acid and concentrated sulfuric acid. The dinitro-containing fused-ring compound **4** was obtained in 83% yield. Using the same method, the desired target compound **7**, which possesses two nitro groups and one nitroamino group, could be achieved in good yield (eqn (b)). In contrast, compound **9**, which is an analogue of compound **4**, was readily synthesized according to the reported method (eqn (c)).<sup>25,26</sup>

### 2.2. Spectral and single-crystal X-ray diffraction analysis of energetic compounds

Energetic compounds **4**, **7** and **9** were fully characterized by multinuclear NMR spectroscopy, IR spectroscopy, and



Scheme 1 Preparation of energetic compounds **4**, **7** and **9**.

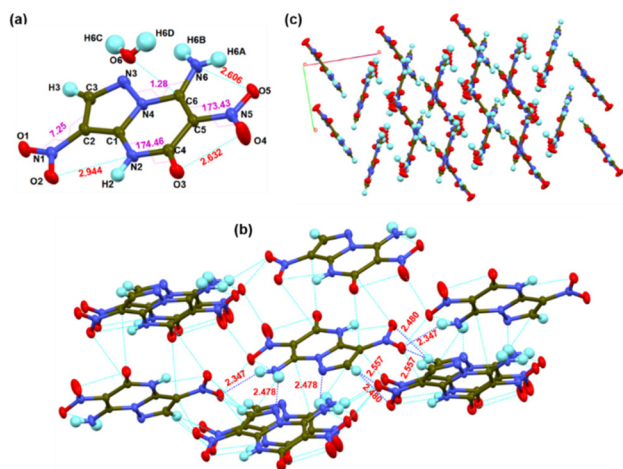
elemental analysis. In the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra, the carbon signals of the carbonyl group in compounds **4** and **7** were observed at 154.23 ppm and 154.09 ppm, respectively. The signals of six carbon atoms, which are directly connected with the nitro groups, were in the range of 111.83–124.22 ppm. It should be noted that the signal of the carbon atom connected to the amino group in compound **9** (152.44 ppm) shifts to a lower field than those of compounds **4** (149.16 ppm) and **7** (148.98 ppm). Single crystals meeting the test standards for X-ray diffraction studies were obtained by the slow evaporation of solutions of DMSO (**4** and **7**) or acetonitrile (**9**).

Compound **4**· $\text{H}_2\text{O}$  crystallizes in the monoclinic crystal system and  $P2_1/n$  space group with four moieties per unit cell ( $Z = 4$ ) and a calculated density of  $1.865\text{ g cm}^{-3}$  at 170 K. The molecular structure of **4**· $\text{H}_2\text{O}$  is shown in Fig. 2a. There are three strong intramolecular interactions (2.606 Å–2.944 Å) formed between N(2) and O(2), N(6) and O(5), O(3) and O(4), respectively. All atoms in compound **4** are nearly coplanar, which could be identified by the torsion angles O(4)–N(5)–C(5)–C(6) =  $173.43^\circ$ , O(3)–C(4)–N(2)–C(1) =  $174.46^\circ$ , O(1)–N(1)–C(2)–C(3) =  $7.25^\circ$ , and N(3)–N(4)–C(6)–N(6) =  $1.28^\circ$ . Each molecule of compound **4** interacts with nine other molecules from three different directions through eight hydrogen bonds and lots of weak associations such as C···O, O···O, and C···C interactions (Fig. 2b). Due to these interactions, compound **4** adopts a cross-like stacking arrangement.

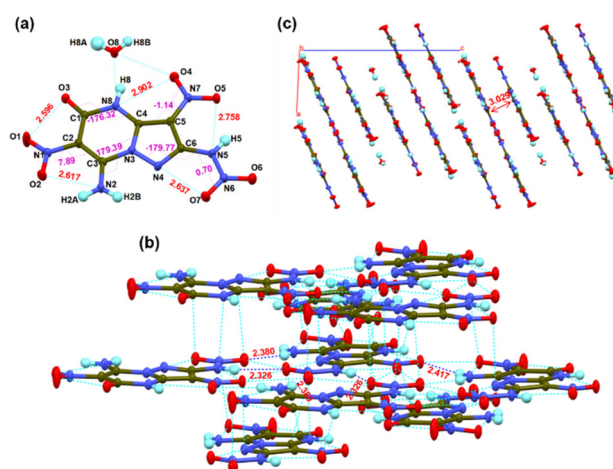
Crystal **7**· $\text{H}_2\text{O}$  crystallizes in the monoclinic space group,  $P2_1/n$ , with four formula units per unit cell ( $Z = 4$ ). The calculated density of **7**· $\text{H}_2\text{O}$  is  $1.989\text{ g cm}^{-3}$  at 100 K. As shown in Fig. 3a, there are five strong intramolecular interactions (2.596 Å–2.902 Å) due to the presence of the nitroamino group, the number of which is more than that in compound **4**. Based on this, the atoms in molecule **7** vibrate less under the external stimuli, making it less likely to produce loca-

lized heating. Similarly, the amino group, two nitro groups, the nitroamino group, and the carbonyl group in compound **7** are almost all coplanar, and some representative torsion angles are O(7)–N(6)–N(5)–C(6) =  $-0.70^\circ$ , N(5)–C(6)–N(4)–N(3) =  $-179.77^\circ$ , C(4)–N(3)–C(3)–N(2) =  $179.39^\circ$ , O(2)–N(1)–C(2)–C(3) =  $7.89^\circ$ , O(3)–C(1)–N(8)–C(4) =  $-176.32^\circ$  and O(4)–N(7)–C(5)–C(4) =  $-1.14^\circ$ . Each molecule mainly interacts with three other molecules in the horizontal direction *via* five hydrogen bonds (2.326 Å–2.417 Å). Notably, the nitroamino group of one molecule is surrounded by three hydrogen bonds, which makes this nitroamino group more stable compared to ordinary ones.<sup>6</sup> In the vertical direction, this molecule associates with six other molecules using various weak interactions, such as N···O, O···O, C···O, and C···N interactions (Fig. 3b). Based on these interactions, the molecules are closely stacked together in a face-to-face manner with a spacing of 3.029 Å, which is less than the typical distance range for  $\pi$ – $\pi$  interactions (3.800 Å) (Fig. 3c).

Compound **9**· $\text{H}_2\text{O}$  belongs to the monoclinic space group  $P2_1/n$  with eight formula units per cell ( $Z = 8$ ) and a crystal density of  $1.768\text{ g cm}^{-3}$  at 170 K (Fig. 4). Due to fewer substituents on the fused-ring than those present in compounds **4** and **7**, there are only two intramolecular interactions (2.692 Å for and 2.933 Å) formed between N(8) and O(2), and N(2) and O(5). However, the amino group, two nitro groups, and the fused-ring of compound **9** are also nearly coplanar with the torsion angles O(4)–N(5)–C(5)–C(4) =  $179.53^\circ$ , N(2)–C(4)–N(3)–N(4) =  $-179.98^\circ$ , O(2)–N(1)–C(2)–C(1) =  $178.57^\circ$ , and N(8)–C(3)–N(3)–C(4) =  $-179.32^\circ$ . As shown in Fig. 4b, although only one conventional hydrogen bond (2.374 Å) could be found from one molecule of **9**, there are three intermolecular weak hydrogen bonds (2.320 Å–2.505 Å) to stabilize the stacking of molecules. Therefore, the molecules form a face-to-face stacking arrangement with a spacing of 3.140 Å.



**Fig. 2** (a) The molecular structure of **4**· $\text{H}_2\text{O}$ . (b) The intermolecular weak interactions of **4**. (c) The packing diagram of **4** viewed along the *c*-axis.



**Fig. 3** (a) The molecular structure of **7**· $\text{H}_2\text{O}$ . (b) The intermolecular weak interactions of **7**. (c) The packing diagram of **7** viewed along the *b*-axis.

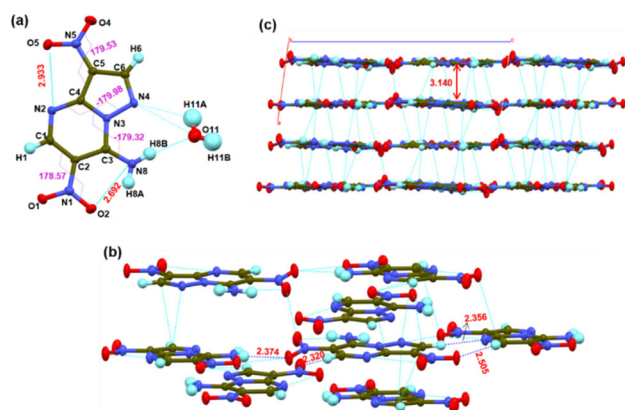


Fig. 4 (a) The molecular structure of **9**·H<sub>2</sub>O. (b) The intermolecular weak interactions of **9**. (c) The packing diagram of **9** viewed along the *b*-axis.

### 3. Physicochemical and energetic properties

The thermal behavior of energetic materials **4**, **7** and **9** was determined through differential scanning calorimetry (DSC) at a heating rate of 5 °C min<sup>−1</sup> (Table 1). The results showed that these compounds decomposed directly without a melting point. Compounds **4**, **7** and **9** had decomposition temperatures (onset) of 287.5 °C, 104.7 °C, and 281.3 °C, respectively. The experimental densities of these three fused-ring compounds were measured by using a gas pycnometer (25 °C). The compound **7** demonstrated excellent density (2.04 g cm<sup>−3</sup>) due to the presence of the nitroamino group and good  $\pi$ – $\pi$  interactions, which is higher than the densities obtained for explosive standards such as **TATB** (1.94 g cm<sup>−3</sup>), **RDX** (1.80 g cm<sup>−3</sup>), and **HMX** (1.91 g cm<sup>−3</sup>). The densities of compounds **4** (1.90 g cm<sup>−3</sup>) and **9** (1.82 g cm<sup>−3</sup>) verified that embedding a carbonyl group into the fused ring increases the density of the resulting compound. Compound **9** has a positive heat of formation (0.83 kJ g<sup>−1</sup>) calculated with Gaussian 09 based on the isodesmic reaction (Fig. S1†). The heat of formation of compounds **4** and **7** are −0.13 kJ g<sup>−1</sup> and 0.83 kJ g<sup>−1</sup>, respectively. Based on the above-measured densities and calculated heats of for-

mation, the detonation velocity and detonation pressure of these three compounds were calculated with the EXPLO 5 (version 6.05) program.<sup>27</sup> As summarized in Table 1, compound **7** possesses excellent detonation performance ( $D_v$  = 8943 m s<sup>−1</sup>,  $P$  = 35.0 GPa) mainly benefiting from its high density, which is superior to that of **RDX** ( $D_v$  = 8795 m s<sup>−1</sup>,  $P$  = 34.9 GPa) and close to the values of **HMX** ( $D_v$  = 9144 m s<sup>−1</sup>,  $P$  = 39.2 GPa).<sup>2</sup> The calculated detonation velocity of compound **4** ( $D_v$  = 7791 m s<sup>−1</sup>) is 291 m s<sup>−1</sup> higher than that of compound **9** ( $D_v$  = 7500 m s<sup>−1</sup>), and the corresponding detonation pressure value for **4** (24.5 GPa) is also 2.3 GPa higher than that of compound **9** (22.2 GPa). As a result, it is easy to deduce that introducing a carbonyl group is an effective method of improving the detonation performance of fused-ring energetic materials. Sensitivities toward impact (IS) and friction (FS) for compounds **4**, **7**, and **9** were measured employing BAM technology.<sup>28</sup> Due to the presence of *o*-amino-nitro and large conjugation systems, all three compounds demonstrated excellent sensitivities (IS > 40 J, FS > 360 N), with the friction sensitivity of compound **9** being over 60 N.

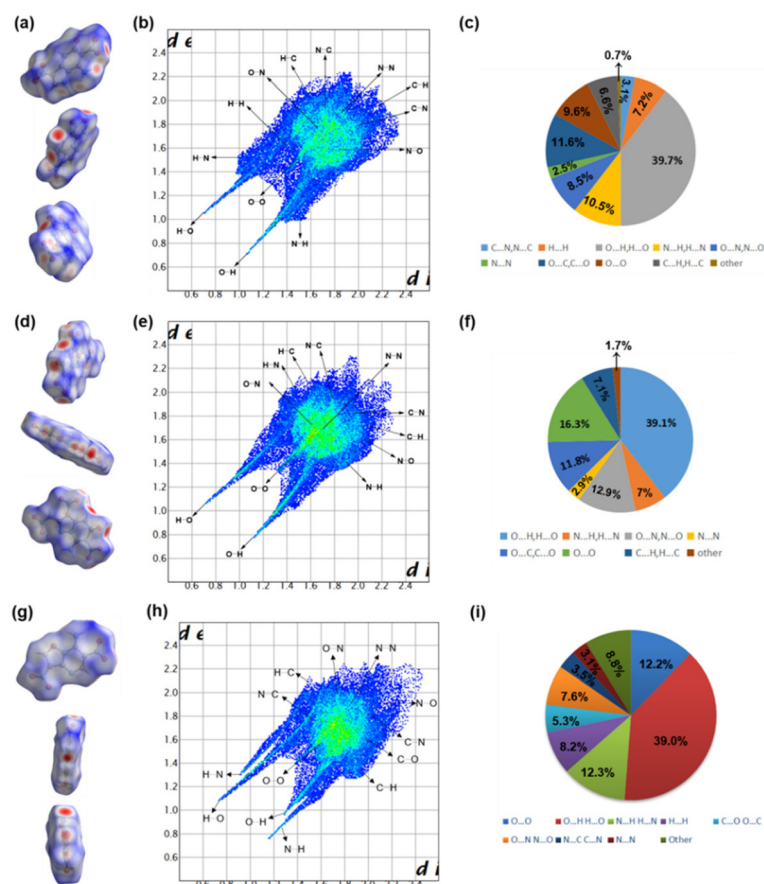
To understand the relationships between the sensitivity and structure, weak interactions in these three energetic compounds were inspected *via* Hirshfeld surfaces and two-dimensional (2D) fingerprint plots.<sup>14</sup> As shown in Fig. 5a, d, and g, all compounds have plate-shaped surfaces due to their coplanar conjugated molecular structures. Some red dots mainly produced by intermolecular hydrogen bonding interactions were observed on the edge of the amino, nitro, carbonyl, nitroamino, and secondary amino groups. The sharp spikes in the 2D fingerprint plots of Fig. 5b, e, and f further confirm the existence of hydrogen bonds, including H...O, O...H, N...H, and H...N interactions. The populations of these weak interactions could also be directly assessed by the 2D fingerprint plots. All three compounds have high ratios of strong and/or weak hydrogen bonding interactions, with the values being 50.2% for **4**, 46.1% for **7**, and 51.3% for **9**. Understandably, compound **7** possesses the highest proportion of O...O interactions (16.3%), because the molecules contain more nitro groups than compounds **4** and **9**. However, the O...O interactions of **4** (9.6%), which contains more oxygen atoms, are fewer than those in compound **9** (12.2%). Based on the crystal structure analysis in Fig. 2–4, it can be inferred that the intramolecular hydrogen bonding between the secondary amino

Table 1 Physicochemical and energetic properties of the synthesized compounds

Comp.	$\rho^a$ (g cm <sup>−3</sup> )	$T_d^b$ (°C)	$\Delta H_f^c$ (kJ mol <sup>−1</sup> /kJ g <sup>−1</sup> )	$D_v^d$ (m s <sup>−1</sup> )	$P^e$ (GPa)	IS <sup>f</sup> (J)	FS <sup>g</sup> (N)
<b>4</b>	1.90	288	−32.0/−0.13	7791	24.5	>40	>360
<b>7</b>	2.04	105	53.61/0.18	8943	35.0	>40	>360
<b>9</b>	1.82	281	173.2/0.77	7500	22.2	>60	>360
<b>TATB</b> <sup>h</sup>	1.94	360	−154.2/−0.60	8544	32.1	50	>360
<b>RDX</b> <sup>h</sup>	1.80	210	70.7/0.32	8795	34.9	7.5	120
<b>HMX</b> <sup>h</sup>	1.91	280	74.8/0.25	9144	39.2	7.0	120

<sup>a</sup> Density (gas pycnometer at 25 °C). <sup>b</sup> Decomposition temperature (onset). <sup>c</sup> Calculated molar enthalpy of formation (solid state). <sup>d</sup> Calculated detonation velocity. <sup>e</sup> Calculated detonation pressure. <sup>f</sup> Impact sensitivity. <sup>g</sup> Friction sensitivity. <sup>h</sup> Ref. 2.





**Fig. 5** Hirshfeld surface calculations of **4**, **7** and **9** as well as two-dimensional fingerprint plots in the crystal structures. Images (a), (d), and (g) are the Hirshfeld surfaces that use color coding to represent the proximity of close contacts around **4**, **7** and **9** molecules (white,  $d$  = van der Waals (vdW) distance; blue,  $d >$  vdW distance; red,  $d <$  vdW distance). The fingerprint plots showing crystal stacking found in **4** (b), **7** (e) and **9** (h). In images (c), (f) and (i), the individual atomic contact percentage contributions to the Hirshfeld surface are shown in the pie chart for **4**, **7** and **9**, respectively.

group and nitro group could interrupt the formation of O...O interactions. In the cooperation of a high hydrogen-bonding ratio and good crystal stacking in compounds **7** and **9**, all the compounds exhibit excellent sensitivity ( $IS > 40$  N,  $FS > 360$  J). Among them, compound **9** was the most insensitive to external stimuli ( $IS > 60$  N,  $FS > 360$  J).

## 4. Conclusions

In summary, two carbonyl-containing energetic materials and their analogues were effectively designed, synthesized and fully characterized by multinuclear NMR, IR and elemental analyses. Their structures were also further confirmed *via* X-ray diffraction. Among these, compound **7** exhibits extremely high density ( $2.04 \text{ g cm}^{-3}$ ), excellent calculated detonation performance ( $D_v = 8943 \text{ m s}^{-1}$ ,  $P = 35.0 \text{ GPa}$ ) and excellent sensitivity ( $IS > 40$  J,  $FS > 360$  N). A detailed comparative study based on X-ray diffraction, Hirshfeld surfaces, and 2D fingerprint plots among compounds **4**, **7** and **9** has further demonstrated that the density and detonation performance could be effectively improved *via* introducing the carbonyl group into fused-ring

compounds. More importantly, the sensitivity of resulting energetic materials was not deteriorated. Obviously, this strategy of introducing carbonyl, *o*-NH<sub>2</sub>-NO<sub>2</sub> and nitroamino groups into fused-ring energetic compounds will help in the design of next-generation high-energy and insensitive energetic materials.

## Author contributions

X. Guo, Y. Feng, and S. Zhi: investigation, methodology, and conceptualization. Y. Fu: manuscript writing. Q. Liu: X-ray data collection and structure solving. Y. Liu and H. Gao: conceptualization, manuscript writing – review and editing, and supervision.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was completed with support from the National Natural Science Foundation of China [No. 22005206, 22075318], the Science and Technology Department of Sichuan Province [No. 2022NSFSC1209, 2022NSFSC0219, 2022NSFSC1263], Vanadium and Titanium Resource Comprehensive Utilization Key Laboratory of Sichuan Province [No. 2021FTSZ08], Sichuan University of Science & Engineering [No. 2022RC11], the Scientific Research and Innovation Team Program of Sichuan University of Science and Engineering [H92307], and the Undergraduate Training Programs for Innovation and Entrepreneurship [No. 202310622009].

## References

- (a) M. H. V. Huynh, M. A. Hiskey, D. E. Chavez, D. L. Naud and R. D. Gilardi, *J. Am. Chem. Soc.*, 2005, **127**, 12537; (b) J.-G. Xu, Y.-F. Yan, X.-Z. Li, F.-K. Zheng and G.-C. Guo, *Chem. Eng. J.*, 2022, **429**, 132451.
- H. Gao, Q. Zhang and J. M. Shreeve, *J. Mater. Chem. A*, 2020, **8**, 4193.
- R. Huisgen and I. Ugi, *Angew. Chem.*, 1956, **68**, 705.
- (a) H. Gao and J. M. Shreeve, *Chem. Rev.*, 2011, **111**, 7377; (b) Q. Lang, Q. Sun, Q. Wang, Q. Lin and M. Lu, *J. Mater. Chem. A*, 2020, **8**, 11752; (c) Z. Yin, W. Huang, Z. Zeng, Y. Liu, J. M. Shreeve and Y. Tang, *ACS Appl. Mater. Interfaces*, 2022, **44**, 49847; (d) S. Banik, P. Kumar, V. D. Ghule, S. Khanna, D. Allimuthu and S. Dharavath, *J. Mater. Chem. A*, 2022, **10**, 22803; (e) Y.-F. Yan, J.-G. Xu, F. Wen, Y. Zhang, H.-Y. Bian, N.-N. Zhang, F.-K. Zheng and G.-C. Guo, *Inorg. Chem. Front.*, 2022, **9**, 5884.
- (a) D. Izsák, T. M. Klapötke, F. H. Lutter and C. Pflüger, *Eur. J. Inorg. Chem.*, 2016, **2016**, 1720; (b) Y. Tang, W. Huang, G. H. Imler, D. A. Parrish and J. M. Shreeve, *J. Am. Chem. Soc.*, 2020, **14**, 7153.
- P. Pagoria, *Propellants, Explos., Pyrotech.*, 2016, **41**, 452.
- (a) J. Wang, Y. Xiong, H. Li and C. Zhang, *J. Phys. Chem. C*, 2018, **122**, 1109; (b) N. U. Zhanpeisov and M. Anpo, *J. Am. Chem. Soc.*, 2004, **126**, 9439; (c) J. Singh, R. J. Staples and J. M. Shreeve, *J. Mater. Chem. A*, 2023, **11**, 12896.
- (a) S. Chen, W. Zhang, Y. Wang and Q. Zhang, *Chem. Eng. J.*, 2021, **421**, 129635; (b) J. Ma, Y. Tang, G. Cheng, G. H. Imler, D. A. Parrish and J. M. Shreeve, *Org. Lett.*, 2020, **22**, 1321; (c) M. C. Schulze, B. L. Scott and D. E. Chavez, *J. Mater. Chem. A*, 2015, **35**, 17963; (d) Y. Liu, G. Zhao, Q. Yu, Y. Tang, G. H. Imler, D. A. Parrish and J. M. Shreeve, *J. Org. Chem.*, 2019, **84**, 16019; (e) A. K. Yadav, V. D. Ghule and S. Dharavath, *J. Mater. Chem. A*, 2022, **10**, 12702; (f) Z. Cheng, Z.-Q. Zhang, Q. Ma, L. Yang, H. Yang, G. Cheng, G. Fan and W. Yang, *Chem. Eng. J.*, 2022, **436**, 131990.
- S. F. Rice and R. L. Simpson, *The unusual stability of TATB: a review of scientific literature*, Livermore CA, USA, 1990.
- Y. Tang, C. He, G. H. Imler, D. A. Parrish and J. M. Shreeve, *ACS Appl. Energy Mater.*, 2019, **2**, 2263.
- Y. Wang, Y. Liu, S. Song, Z. Yang, X. Qi, K. Wang, Y. Liu, Q. Zhang and Y. Tian, *Nat. Commun.*, 2018, **9**, 2444.
- L. Hu, C. He, G. Zhao, G. H. Imler, D. A. Parrish and J. M. Shreeve, *ACS Appl. Energy Mater.*, 2020, **3**, 5510.
- R. Bu, Y. Xiong and C. Zhang, *Cryst. Growth Des.*, 2020, **20**, 2824.
- S. K. Wolff, D. J. Grimwood, J. J. McKinnon, M. J. Turner, D. Jayatilaka and M. A. Spackman, *CrystalExplorer, version 3.1*, University of Western Australia, Crawley, Australia, 2012.
- (a) Y. Tang, D. Kumar and J. M. Shreeve, *J. Am. Chem. Soc.*, 2017, **139**, 13684; (b) D. G. Piercey, D. E. Chavez, B. L. Scott, G. H. Imler and D. A. Parrish, *Angew. Chem., Int. Ed.*, 2016, **55**, 15315.
- Y. Huang, H. Gao, B. Twamley and J. M. Shreeve, *Chem. – Eur. J.*, 2009, **15**, 917.
- J. Sayer and P. Conlon, *J. Am. Chem. Soc.*, 1980, **102**, 3592.
- R. R. Sirach and P. N. Dave, *Chem. Heterocycl. Compd.*, 2021, **57**, 720.
- J. Cai, J. Zhang, J. Xiong, R. Li, T. Fei, Q. Lai, P. Yin and S. Pang, *Chem. Eng. J.*, 2023, **467**, 143527.
- G. Zhao, P. Yin, D. Kumar, G. H. Imler, D. A. Parrish and J. M. Shreeve, *J. Am. Chem. Soc.*, 2019, **141**, 19581.
- B.-J. Zhao, P. Wang, W. Fu, C. Li and Z.-M. Zhou, *ChemistrySelect*, 2018, **3**, 4797.
- (a) Z. Wang, B. Zhao, Y. Liu and J.-P. Wan, *Adv. Synth. Catal.*, 2022, **364**, 1508; (b) B. Kaewmee, V. Rukachaisirikul and J. Kaebamrung, *Org. Biomol. Chem.*, 2017, **15**, 7387.
- Y. Makisumi, *Chem. Pharm. Bull.*, 1962, **10**, 612.
- L. He, H. Pei, L. Ma, Y. Pu, J. Chen, Z. Liu, Y. Ran, L. Lei, S. Fu, M. Tang, A. Peng, C. Long and L. Chen, *Eur. J. Med. Chem.*, 2014, **87**, 595.
- D. A. Gazizov, E. B. Gorbunov, G. L. Rusinov, E. N. Ulomsky and V. N. Charushin, *ACS Omega*, 2020, **5**, 18226.
- Z. Zeng, Y. Liu, Q. Lv, W. Huang, H. Yang, G. Cheng and Y. Tang, *Chem. Eng. J.*, 2022, **450**, 138094.
- M. Sucéska, *EXPLO5, Version 6.01*, Brodarski Institute, Zagreb, Croatia, 2013.
- U. M. Regulations, *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, United Nations Publication, New York, 5th edn, 2009.