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# Nitramino-functionalized Tetracyclic Oxadiazoles as Energetic Materials with High Performance and High Stability: Crystal Structures and Energetic Properties

Qi Sun, Qiuhan Lin\*, and Ming Lu\*

A series of tetracyclic energetic materials are developed through the introduction of 1,2,4-oxadiazole into nitramino-1,2,5oxadiazole. All these thirteen new compounds were fully characterized and seven of them were further confirmed by single crystal X-ray diffraction. Salt formation leads to the planarization of the parent structure, the shortening in length and increase in bond-dissociation energies for N-NO2 bonds, and the formation of hydrogen bonds, which obviously increases the decomposition temperatures from 84 °C (the neutral compound) to 187-303 °C (the energetic salts). The increases fall into the range of 103-219 °C, in which, to the best of our knowledge, 219 °C is the largest reported increase in thermal stability due to salt formation. In addition, electrostatic surface potentials and noncovalent interactions ( $\pi$ - $\pi$ stacking) are analyzed to understand the structure-property relationships of these compounds. Both theoretical calculations and the practical explosive experiment indicate the dihydroxylammonium salt exhibits better detonation performance than powerful explosive RDX. The tetracyclic backbones promises these compounds with enhanced security. The short synthetic steps, low cost, good thermostability, excellent detonation performance, and acceptable mechanical sensitivities highlight the practical applications of these energetic compounds.

### Introduction

High-energy-density materials (HEDMs) are widely used in military and civilian applications as explosives, propellants, and pyrotechnics.<sup>1</sup> Preparing more powerful, safer, and greener energetic materials is a key target of researchers around the world, and the key goal is to balance between the opposing properties of high performance and high stability.<sup>2</sup>

Combining various energetic groups with different backbones is a useful strategy for designing new energetic molecules with tailorable properties.<sup>3</sup> Among the candidate energetic groups, the nitramino group has exceptional properties, which can impart outstanding detonation performance to energetic compounds,<sup>4</sup> while, among the heterocyclic rings, 1,2,5-oxadiazole (furazan) is a promising candidate owing to its high nitrogen and oxygen contents. Therefore, nitramino-functionalized furazans are an effective route toward high-performance energetic materials.<sup>6</sup> 3,4-Di(nitramino)furazan (a in Scheme 1), which consists of two nitramino groups and a 1,2,5-oxadiazole ring, exhibits

excellent detonation performance (D: 9376 m s<sup>-1</sup>, P: 40.5 GPa).<sup>7</sup> In addition, 3,3'-dinitramino-4,4'-bifurazan (**b** in Scheme 1) includes two 1,2,5-oxadiazole rings, it still possesses good detonation performance (D: 9086 m s<sup>-1</sup>, P: 40.3 GPa).<sup>8</sup>

However, the mono, bi, and tricyclic nitramino-furazans show undesirably high sensitivities. For example, a and b have high impact sensitivity (IS) of <1 J and 1.5 J, respectively, and friction sensitivity (FS) of <5 N and 48 N, respectively. Especially, the tricyclic compound c is even unstable in air.<sup>9</sup> These greatly limit their practical applications. Thus, nitraminofurazans with relatively higher mechanical and thermal stabilities are highly sought. In addition, although there are many reports on mono, bi, and tricyclic nitramino-furazans, the tetracyclic nitramino-furazans are rarely reported.<sup>10</sup>

Recent years, introducing different heterocyclic rings into

	1,2,5-oxadiazo	1,2,4- and 1,2,5-oxadiazole Tetracyclic		
Monocyclic Bicyclic				
a	b	c	This work	
O2N-NH HN-NO			02N-NH N-O NH N-O	
IS: <1 J FS: <5 N	IS: 1.5 J FS: 48 N	Not stable in air	IS: 16 J Lower sensitivities FS: 180 N Safer explosives	
Scheme 1. C	omparision	of the mechanical s	tabilities of nitramino-	
functionaliza	d ovadiazal		2.4 avadiasala	



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the structures has been an effective method to modify the energetic properties.<sup>11</sup> In this study, 1,2,4-oxadiazole was introduced into the nitramino-furazan, and a series of nitramino-functionalized furazans with tetracyclic backbones are explored.

### Preparation

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As shown in Scheme 2, 3-amino-4-amidoximinofurazan was prepared through the reaction of malononitrile, sodium nitrite, and hydroxylamine; this was then reacted with diethyl oxalate to obtain compound 1.<sup>12</sup> 1 was then reacted with fuming HNO<sub>3</sub> at 0 °C to obtain compound 2. Twelve energetic salts based on 2 were prepared in high yields via simple acid-base reactions. These salts can be divided into three types according to their cations, viz., monovalent cations, divalent cations, and metal cations. These compounds were fully characterized using infrared spectroscopy, <sup>1</sup>H and <sup>13</sup>C spectroscopy, and elemental analysis.

It is worthy to note that all the reagents are commercially available and cheap. Furthermore, the synthesis conditions are mild and the product purification is very simple. These contributes impart these compounds with considerable potential for practical applications.

### **Crystal structure analysis**

Crystals of selected compounds are obtained to confirm the accuracy of the molecular structures and to explore the potential relationship between the molecular structures and physicochemical properties. Crystals were prepared through slow evaporation in related solutions ( $2 \cdot 2H_2O$  in a mixture of methanol and water; **5**,  $6 \cdot 2H_2O$ , **9**, **10**,  $11 \cdot H_2O$ , and **14** in water) and were tested at 173 K. CCDC numbers of these crystals are 1816899-1816905 and details of crystallographic data are provided in supporting information.

With two crystal water, compound  ${\bf 2}$  crystallized in the orthorhombic crystal system with the Pbca space group, and



Figure 1. Crystal structure of 2.2H<sub>2</sub>O.



**Figure 2.** (a) Crystal structure of **5**, (b) Packing diagram of **5** viewed down the b axis. The sky-blue lines indicate hydrogen bonds.

### Table 1. Hydrogen bonds for 5.

, ,				
D-H···A	D-H/Å	H…A/Å	D…A/Å	D-H…A/°
05-H5…O3	0.826	1.849	2.674	178.10
N7-H7A…N1	0.920	2.302	3.078	141.88
N7-H7A…N5	0.920	2.407	3.079	129.92
N7-H7B…N3	0.915	2.019	2.898	160.43
N7'-H7C'…O3'	0.929	1.982	2.815	148.16

there are four molecules in an asymmetric unit. As can be seen from Figure 1, the whole molecule is symmetric, in other words, the left part is equal to the right part. Four oxadiazole rings are almost coplanar, which is evident from the C3-C4-C1-N2 (170.45°) and O1-C2-C2'-O1' (-180.00°) torsion angles. The N6-N5-C3-C4 (-69.03°) torsion angle indicates the nitro group is out of the oxadiazole plane.

Crystal structure and packing diagram of the monovalent cation organic salt **5** are presented in Figure 2. Different with the parent compound **2**, the dihydroxylammonium salt (**5**) crystallized in the monoclinic crystal system with the P2<sub>1</sub>c space group, and there are two molecules in an asymmetric unit. The whole salt is symmetric too, and the four oxadiazole is more coplanar than **2**, which can be seen from the C3-C4-C1-N2 (177.35°) and O1-C2-C2'-O1' (-180.00°) torsion angles. In addition, the salt formation also makes the nitro group nearly coplanar with the oxadiazole plane, the torsion angle of N6-

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N5-C3-C4 is 175.78°. As is shown in Figure 2(b), there are five pairs of hydrogen bonds were found in the packing system. All hydrogen atoms in the hydroxylamine cation form hydrogen bonds with acceptor atoms (N and O) in the anion. The bond lengths and angles are provided in Table 1. The shortest distance of hydrogen-acceptor (H···A) in this salt is H5···O3, and the length is 1.849 Å, which is shorter than the average shortest H···A distance (1.893 Å) in reported energetic salts. Such a short length of the hydrogen bond reveals the close packing of the cations and anions, which then leads to a high crystal density of 1.880 g cm<sup>-3</sup>. Furthermore, these extensive hydrogen-bonding interactions will also contribute to the improvement of thermal stability and mechanical sensitivities.

Molecular structures of other organic salts, including monovalent cation salts  $6\cdot 2H_2O$ , 9, and 10 and divalent cation salt  $11\cdot H_2O$ , are presented in Figure 3, while the packing diagrams with hydrogen bonds are presented in supporting information. It is interesting that all these four salts crystallized in the same monoclinic crystal system, and the same P2<sub>1</sub>c space group with compound **5**. Also, the anions in these salts



Figure 3. (a), (b), (c) and (d) Crystal structures of  $6 \cdot 2H_2O$ , 9, 10, and  $11 \cdot H_2O$ .



Figure 4. (a) Coordination environment of 14, (b) Packing diagram of 3D metal-organic-framework of 14.

are planar structures and symmetric. Due to the difference of cations and crystal waters, they exhibit different crystal densities, and the values are 1.774, 1.790, 1.762, and 1.827 g cm<sup>-3</sup>, respectively.

Different with organic salts, the inorganic dipotassium salt **14** (Figure 4) crystallized in the Triclinic P-1 space group, and there is one potassium cation and half anion in each asymmetric unit. The crystal density at 173 K is 2.043 g cm<sup>-3</sup>, which is obviously higher than those of organic salts (1.762-1.880 g cm<sup>-3</sup>). Each anion is coordinated with ten potassium ions, while each potassium cation is coordinated with five anions. The bond lengths of K-N and K-O fall in the range of 2.665-3.265 Å. The whole packing system indicates compound **14** exhibit a 3D-metal-organic framework (Figure 5b), which promotes the increase of thermal stability and density.

### Thermal stability

Thermal stability is a key property for energetic materials. In this study, this was measured using differential scanning calorimetry (DSC) with a ramp rate of 5 °C min<sup>-1</sup>. It should be noted that all the sample were put in the oven at 60 °C for 12 h to make sure that there is no crystal water remained. Values for decomposition temperatures are provided in Table 2 and DSC plots for selected compounds (2, 5, 7, and 13) are provided in Figure 5. None of the compounds melt before decomposition. Although compound 2 has a decomposition temperature of 84 °C, its salts have much better thermal stabilities (T<sub>d</sub>: 187-303 °C). Among the organic salts, the dihydroxylammonium salt (5) has the lowest decomposition temperature ( $T_d$ : 187 °C), while the diguanidinium salt (7) has the highest decomposition temperature (T<sub>d</sub>: 263 °C). Both metal salts have higher thermal stabilities (T<sub>d</sub>: 274 °C and 303 °C) than the organic salts (T<sub>d</sub>: 187-303 °C).

In many cases, salt formation can improve the thermostability of energetic compounds. In this study, the increases in decomposition temperature are in the range of



Figure 5. DSC plots for compounds 2, 5, 7, and 13.

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Figure 6. (a) Structure changes of the neutral molecule 2 (b) Bond lengths of N-NO2 (c) Bond-dissociation energies for N-NO2.



Figure 7. Noncovalent interaction analysis, including HB (hydrogen bonds) and  $\pi$ - $\pi$  interactions for 2 (a) and 5 (b).



Figure 8. Electrostatic potential surfaces of 2 (a) and 5 (b). The minimum and maximum of ESP are marked as blue and red points, respectively. The maximum value of ESP around nitramino groups are labeled by red texts, the units are in kcal/mol.

103-219 °C. To the best of our knowledge, 219 °C is the largest reported increase in thermal stability due to salt formation. To investigate the reasons for this phenomenon, further study on the X-ray data were performed. Two possible explanations are suggested.

First, there is an increase in the bond-dissociation energies (BDEs) for the weakest bonds, N5-N6/N-NO<sub>2</sub>. The weakest chemical bond breaks first during decomposition and, in this case, calculations indicate that the N-NO<sub>2</sub> bond is the weakest. Owing to salt formation, the nonplanar compound **2** was transformed into a planar structure (Figure 6a), resulting in a decrease in the N-NO<sub>2</sub> bond lengths (Figure 6b). BDEs for the N5-N6 bonds of the selected compounds are presented in Figure 6c. The values of the lengths and BDEs are provided in ESI. The nonplanar compound **2** exhibits the lowest BDE (159.7 kJ mol<sup>-1</sup>), while the others possess much higher BDEs (310.7-381.5 kJ mol<sup>-1</sup>), meaning the salts are more stable.

Second, there are extensive hydrogen-bonding interactions between the cations and anions. Owing to the high numbers of N and O atoms in the anion and H atoms in the cations, it is likely that numerous hydrogen bonds will be formed. The details of these (H-bonding diagrams, bond lengths and angles) are provided in the ESI. Noncovalent interaction analysis (Figure 7) also indicates the existence of hydrogen bonds in salts (Figure 7b). In addition, the electrostatic surface potentials (ESPs) of the neutral compound 2 and salt 5 are studied to understand the bond stability before and after the formation of the hydrogen bonds. As shown in Figure 8, salt 5 possesses lower maximum ESP values than the neutral compound 2 does, which indicates the significant influence of H-bonding on the electrostatic potential. Furthermore, there is increased electron density around the N-NO<sub>2</sub> bond upon salt formation, shortening the N-NO<sub>2</sub> bond, increasing the

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corresponding BDE, and, consequently, improving the thermostability.

### **Energetic properties**

Densities, heats of formation, detonation velocities and pressures, and mechanical sensitivities are also studied to evaluate the suitability of these compounds as HEDMs.

The densities of these tetracyclic oxadiazoles fall into the range of 1.668-1.973 g cm<sup>-3</sup>, and the dipotassium salt (14) shows the highest density by a significant margin. Besides the metal salts, the dihydroxylammonium salt (5) exhibits the highest density of 1.870 g cm<sup>-3</sup>, which is much higher than that of RDX (1.800 g cm<sup>-3</sup>). It is notable that even salt **5** has a higher density than the neutral compound **2** (1.853 g cm<sup>-3</sup>). As is shown in Figure 7, salt **5** exhibits more  $\pi$ - $\pi$  interactions and hydrogen bonds than compound **2**, which may be the cause of the higher density.

Heats of formation were calculated by Gaussian  $09^{13}$ , and the details are shown in ESI. Owing to the existence of extensive high-energy N-N, C-N and N-O bonding, all the compounds studied exhibit high positive values in the range of 355.2-1345.2 kJ mol<sup>-1</sup> (0.76-2.39 kJ g<sup>-1</sup>), much higher than those of RDX and HMX.

Detonation performance, including detonation velocities and pressures, is evaluated using EXPLO5.<sup>14</sup> Among the organic materials (2-12), because of its highest density and second best oxygen balance, the dihydroxylammonium salt (5) possesses the best detonation performance (D: 9030 m s<sup>-1</sup>, P: 36.0 GPa), which is superior to RDX (D: 8795 m s<sup>-1</sup>, P: 34.9 GPa) and slightly poor than HMX (D: 9144 m s<sup>-1</sup>, P: 39.2 GPa). Besides compound 5, the neutral compound (2) and



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Figure 9. (a) Equipment of the explosion experiment. (b) Abridged general view of the equipment. (c) and (d) Holes caused by explosion of salt 5 and RDX.

dihydrazinium salt (4) also show comparable detonation performance (D: 8793 and 8836 m s<sup>-1</sup>, P: 33.0 and 33.3 GPa) to RDX.

In order to further understand the practical detonation performance of **5**, the explosive experiment was performed. As shown in Figure 9, 450 mg of **5** was filled in the equipment, and was initiated by using 60 mg lead azide. Furthermore, a contrast experiment was also performed to compare the detonation performance of RDX and **5**. The results show that the diameter (12.1 mm) of lead hole caused by **5** is larger than that (11.6 mm) of RDX, in other words, **5** is really more powerful than RDX.

The IS and FS of these materials were also measured to

Table 2. Physical properties and energetic performance of compounds 2-14 compared with RDX and HMX.									
Compd	Τ <sub>d</sub> <sup>a</sup>	ΔTd <sup>b</sup>	dc	N+O <sup>d</sup>	$\Delta H_{f}^{e}$	D <sup>†</sup>	P <sup>g</sup>	IS <sup>h</sup>	FS
	[°C]	[°C]	[g cm⁻³]	[%]	[kJ mol <sup>-1</sup> / kJ g <sup>-1</sup> ]	[m s <sup>-1</sup> ]	[GPa]	[J]	[N]
2	84	_	1.853	75.1	786.3/1.99	8793	33.3	16	180
3	215	131	1.755	75.7	614.9/1.44	8343	28.8	20	240
4	225	141	1.819	76.8	910.5/1.99	8836	33.0	12	160
5	187	103	1.870	77.4	699.8/1.52	9030	36.0	12	180
6	225	141	1.785	73.3	1014.6/1.71	8315	27.2	40	>360
7	263	179	1.668	74.2	607.5/1.19	7838	23.2	36	360
8	228	144	1.703	75.2	804.9/1.48	8151	25.5	>40	>360
9	221	137	1.755	72.6	1345.2/2.39	8325	27.9	14	160
10	218	134	1.730	72.6	1087.9/1.93	8078	25.7	22	220
11	191	107	1.798	76.0	487.3/1.01	8339	29.2	20	180
12	198	114	1.774	74.8	553.0/1.09	8080	26.0	18	180
13	303	219	1.887	67.6	511.1/1.17	_	_	20	280
14	274	190	1.973	63.0	355.2/0.76	_	_	36	>360
RDX <sup>k</sup>	230	_	1.800	81.1	92.6/0.42	8795	34.9	7.4	120
HMX <sup>k</sup>	280	_	1.905	811	70.4/0.25	9144	39.2	7.4	120

<sup>a</sup> Thermal decomposition temperature (onset, 5 °C min<sup>-1</sup>). <sup>b</sup> Increase of thermal stability. <sup>c</sup> Density (measured by gas pycnometer, 298 K). <sup>d</sup> Content of nitrogen and oxygen. <sup>e</sup> Heats of formation. <sup>f</sup> Detonation velocity. <sup>g</sup> Detonation pressure. <sup>h</sup> Impact sensitivity. <sup>i</sup> Friction sensitivity. <sup>j</sup> Ref 6d.

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**Figure 10.** Changes of different crystal packings with or without external mechanical force.

evaluate their safety.<sup>16</sup> Due to the tetracyclic backbone, all new materials show better mechanical stability than RDX and HMX. The neutral compound (2) exhibits acceptable mechanical sensitivities (IS: 16 J, FS: 180 N), which is a significant improvement than those reported one-, two- or three-ring nitramino-furazan. The extensive H-bonding interactions between cations and anions also contribute the organic salts (3-12) show good mechanical stability. It is unexpected that salt 5 is more sensitive than compound 2. According to results presented in Figures 6-8, 2 has nonplanar structure, weak  $\pi$ - $\pi$  stacking interactions and less electron density around N-NO<sub>2</sub>, which indicates that 2 should show a relatively poor sensitivity. In fact, the mechanical sensitivities are related to many factors. Not only the molecular structures, hydrogen bonds, and so on, the whole packing system also influences the mechanical sensitivities. X-ray data indicate that 2 exhibits a wavelike stacking, while 5 exhibit a cross stacking. As shown in figure 10, when the compounds suffer from external force, the packing system may form a certain shape change. When this change comes to the limitation, decompositon of energetic materials will happen. It is clear that 5 is easier to reach the limitation than 2 is, which may lead to relatively lower sensitivities. In addition, the metal salts (13 and 14) are insensitive, especially, the dipotassium salt (14) exhibit the IS of 36 J and FS of >360 N. This may be explained by the tetracyclic backbone and the special 3D metal-organic framework of 14.

### Conclusions

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In summary, we investigated the preparation, structural characterization, physical properties, and energetic performance of thirteen new nitramino-functionalized tetracyclic oxadiazoles. According to the X-ray data, salt formation leads to the planarization of the parent structure, the shortening in lengths and increase in the BDEs of the N-NO<sub>2</sub> bonds, and the formation of hydrogen bonds, which increase the decomposition temperatures from 84 °C (the neutral compound) to 187-303 °C (the energetic salts). Noncovalent interactions and electrostatic potential surfaces are studied to better understand the improvement of thermal stability.  $\pi$ - $\pi$  stacking results in salt 5 having a higher density than the neutral compound (2). Owing to the presence of highenergy N-N and N-O bonds, these compounds show high heats of formation (355.2-1345.2 kJ mol<sup>-1</sup>). The calculated detonation performances and explosive tests indicate compound **5** is obviously better than RDX. More importantly, through the introduction of 1,2,4-oxadiazole, these tetracyclic oxadiazoles show better mechanical stabilities than mono, bi or tricyclic nitramino-furazans, RDX, and HMX. These favorable results indicate that combination of 1,2,4-oxadiazole and nitramino-1,2,5-oxadiazole is a promising strategy for designing energetic materials.

### **Experimental section**

Details of all the experiments can be found in the ESI.

### Attention

Although there were no explosion found in our operation, all presented compounds show the possibility of explosion, very careful treatments are needed.

### Syntheses

### N,N'-([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diylbis(1,2,5-oxadiazole-

**4,3-diyl))dinitramide (2).** Compound **1** (3.04 g, 10 mmol) was added slowly in 95% HNO<sub>3</sub> (6 ml) at 0 °C. After 1 hour, the mixture was poured in ice water (200 ml) and the insoluble matter precipitates out. The precipitate was filtered to get compound **2** (2.88 g, yield: 73.0 %). Light yellow solids. T<sub>d</sub>: 84 °C. <sup>1</sup>H NMR (500 MHz, d6-DMSO):  $\delta$  7.08 (s) ppm. <sup>13</sup>C NMR (500 MHz, d6-DMSO):  $\delta$  163.84, 159.74, 152.87, 141.94 ppm. IR (KBr):  $\upsilon$  3471, 2728, 1979, 1690, 1621, 1595, 1514, 1460, 1321, 1237, 1167, 1038, 977, 872, 800, 761, 679 cm<sup>-1</sup>. Elemental analysis for C<sub>8</sub>H<sub>2</sub>N<sub>12</sub>O<sub>8</sub> (394.18): calcd C 24.38, H 0.51, N 42.64%. Found: C 24.53, H 0.57, N 42.42%.

### General methods for preparing compounds 3-14:

28% aqueous ammonia (1.20 g, 20 mmol), 98% hydrazine monohydrate (1.02 g, 20 mmol), 50% hydroxylamine solution (1.32 g, 20 mmol), 3,5-diamino-1,2,4-triazole (1.98 g, 20 mmol), guanidine carbonate (1.80 g, 10 mmol), aminoguanidine bicarbonate (2.68 g, 20 mmol), 4-amino-1,2,4-triazole (1.66 g, 20 mmol), 3-amino-1,2,4-triazole (1.66 g, 20 mmol), carbohydrazide (0.91 g, 10 mmol), 4-Amino-3-hydrazino-1,2,4-triazole (1.15 g, 10 mmol), sodium hydroxide (0.8 g, 20 mmol), and potassium hydroxide (1.12 g, 20 mmol) were added slowly into the **2** (3.94 g, 10 mmol) acetonitrile (20 ml) solution respectively. The precipitate was filtered to get energetic salts 3-14.

Diammonium ([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diylbis(1,2,5-oxadiazole-4,3-diyl))bis(nitroamide) (3). Yellow solids (3.67 g, yield: 85.7%). T<sub>d</sub>: 215 °C. <sup>1</sup>H NMR (500 MHz, d6-DMSO): δ 7.14 (s) ppm. <sup>13</sup>C NMR (500 MHz, d6-DMSO): δ 163.48, 160.67, 158.23, 141.36 ppm. IR (KBr): υ 3600, 3194, 1596, 1525, 1503, 1411, 1288, 1184, 1138, 1040, 971, 911, 820, 778, 767 cm<sup>-1</sup>. Elemental analysis for  $C_8H_8N_{14}O_8$  (428.24): calcd C 22.44, H 1.88, N 45.79%. Found: C 22.27, H 1.76, N 45.94%.

Dihydrazium([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diylbis(1,2,5-<br/>oxadiazole-4,3-diyl))bis(nitroamide) (4). Yellow solids (3.95 g, yield:<br/>86.3%). T<sub>d</sub>: 225 °C. <sup>1</sup>H NMR (500 MHz, d6-DMSO): δ 7.09 (br) ppm.<br/><sup>13</sup>C NMR (500 MHz, d6-DMSO): δ 163.45, 160.64, 158.04, 141.25<br/>ppm. IR (KBr): υ 3184, 1595, 1526, 1501, 1431, 1365, 1283, 1176,

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1136, 1039, 970, 911, 876, 820, 766, 737 cm<sup>-1</sup>. Elemental analysis for  $C_8H_{10}N_{16}O_8$  (458.27): calcd C 20.97, H 2.20, N 48.90%. Found: C 20.77, H 2.11, N 49.03%.

Dihydroxylammonium([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diylbis(1,2,5-oxadiazole-4,3-diyl))bis (nitroamide) (5). Yellow solids(3.83 g, yield: 82.9%). T<sub>d</sub>: 187 °C. <sup>1</sup>H NMR (500 MHz, d6-DMSO): δ9.98 (s) ppm. <sup>13</sup>C NMR (500 MHz, d6-DMSO): δ163.44, 160.67,158.21, 141.39 ppm. IR (KBr): v2952, 2725, 1599, 1525, 1503, 1433,1391, 1284, 1176, 1136, 1010, 972, 918, 820, 766, 737 cm<sup>-1</sup>.Elemental analysis for C<sub>8</sub>H<sub>8</sub>N<sub>14</sub>O<sub>10</sub> (460.24): calcd C 20.88, H 1.75, N42.61%. Found: C 20.73, H 1.61, N 42.74%.

 $\begin{array}{l} \label{eq:constraint} \textbf{Di(3,5-diamino-1,2,4-triazolium)} ([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diylbis(1,2,5-oxadiazole-4,3-diyl)) bis(nitroamide) (6). Yellow solids (5.02 g, yield: 84.8%). T_d: 225 °C. <math display="inline">^1\text{H}$  NMR (500 MHz, d6-DMSO):  $\delta$  163.42, 160.69, 158.33, 151.25, 141.45 ppm. IR (KBr):  $\upsilon$  3293, 3159, 2756, 1694, 1651, 1595, 1524, 1415, 1384, 1303, 1175, 1018, 971, 914, 875, 767, 715 cm  $^{-1}$ . Elemental analysis for C12H12N22O8 (592.34): calcd C 24.33, H 2.04, N 52.02%. Found: C 24.46, H 1.98, N 51.93%.

Diguanidinium([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diylbis(1,2,5-<br/>oxadiazole-4,3-diyl))bis(nitroamide) (7). Yellow solids (4.19 g, yield:<br/>81.9%). T<sub>d</sub>: 263 °C. <sup>1</sup>H NMR (500 MHz, d6-DMSO): δ 6.97 (s) ppm.<br/><sup>13</sup>C NMR (500 MHz, d6-DMSO): δ 163.43, 160.67, 158.20, 157.98,<br/>141.42 ppm. IR (KBr): υ 3404, 3340, 3255, 3196, 1652, 1601, 1517,<br/>1498, 1413, 1388, 1286, 1187, 1139, 1044, 970, 911, 819 cm<sup>-1</sup>.<br/>Elemental analysis for  $C_{10}H_{12}N_{18}O_8$  (512.32): calcd C 23.44, H 2.36, N<br/>49.21%. Found: C 23.57, H 2.43, N 49.03%.

Di(aminoguanidinium) ([5,5'-bi(1,2,4-oxadiazole)]-3,3'diylbis(1,2,5-oxadiazole-4,3-diyl))bis (nitroamide) (8). Yellow solids (4.67 g, yield: 86.1%). T<sub>d</sub>: 228 °C. <sup>1</sup>H NMR (500 MHz, d6-DMSO): δ 8.60 (s), 7.26 (s), 6.68 (s), 4.68 (s) ppm. <sup>13</sup>C NMR (500 MHz, d6-DMSO): δ 163.45, 160.59, 158.81, 158.31, 141.46 ppm. IR (KBr): u 3446, 3308, 3202, 1662, 1588, 1525, 1497, 1425, 1290, 1171, 1132, 1040, 968, 920, 837, 819,766 cm<sup>-1</sup>. Elemental analysis for C<sub>10</sub>H<sub>14</sub>N<sub>20</sub>O<sub>8</sub> (542.35): calcd C 22.15, H 2.60, N 51.65%. Found: C 22.02, H 2.61, N 51.74%.

**Di(4-amino-1,2,4-triazolium)** ([5,5'-bi(1,2,4-oxadiazole)]-3,3'diylbis(1,2,5-oxadiazole-4,3-diyl))bis (nitroamide) (9). Yellow solids (4.73 g, yield: 84.2%). T<sub>d</sub>: 221 °C. <sup>1</sup>H NMR (500 MHz, d6-DMSO): δ 9.50 (s) ppm. <sup>13</sup>C NMR (500 MHz, d6-DMSO): δ 163.48, 160.59, 157.75, 144.09, 141.42 ppm. IR (KBr): υ 3583, 3320, 3122, 3011, 1592, 1500, 1424, 1398, 1261, 1216, 1154, 963, 938, 863, 811, 767, 715 cm<sup>-1</sup>. Elemental analysis for C<sub>12</sub>H<sub>10</sub>N<sub>20</sub>O<sub>8</sub> (562.34): calcd C 25.63, H 1.79, N 49.82%. Found: C 25.51, H 1.72, N 50.01%.

Carbonicdihydrazidinium([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diylbis(1,2,5-oxadiazole-4,3-diyl))bis(nitroamide)(11).solids(4.00 g, yield: 82.6%).T<sub>d</sub>: 191 °C. <sup>1</sup>H NMR (500 MHz, d6-DMSO): δ10.32 (s), 8.33 (s) ppm. <sup>13</sup>C NMR (500 MHz, d6-DMSO): δ163.45, 160.62, 157.96, 156.78, 141.46 ppm. IR (KBr): υ 3501, 2950,

2743, 1755, 1591, 1564, 1523, 1434, 1289, 1173, 1137, 1014, 970, 920, 880, 827, 766 cm<sup>-1</sup>. Elemental analysis for  $C_9H_8N_{16}O_9$  (484.27): calcd C 22.32, H 1.67, N 46.28%. Found: C 22.27, H 1.71, N 46.43%.

4-Amino-3-hydrazino-1,2,4-triazolium ([5,5'-bi(1,2,4oxadiazole)]-3,3'-diylbis(1,2,5-oxadiazole-4,3- iyl))bis(nitroamide) (12). Yellow solids (4.34 g, yield: 85.4%). T<sub>d</sub>: 198 °C. <sup>1</sup>H NMR (500 MHz, d6-DMSO): δ 9.81 (s) ppm. <sup>13</sup>C NMR (500 MHz, d6-DMSO): δ 163.45, 160.79, 158.22, 152.70, 142.83, 141.38 ppm. IR (KBr): υ 3366, 3190, 1741, 1703, 1643, 1594, 1519, 1424, 1323, 1174, 1133, 1084, 1038, 970, 914, 826, 766 cm<sup>-1</sup>. Elemental analysis for C<sub>10</sub>H<sub>8</sub>N<sub>18</sub>O<sub>8</sub> (508.29): calcd C 23.63, H 1.59, N 49.60%. Found: C 23.51, H 1.64, N 49.75%.

 $\begin{array}{c} \textbf{Disodium} & ([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diylbis(1,2,5-oxadiazole-4,3-diyl))bis(nitroamide) (13). Yellow solids (3.68 g, yield: 3.68%). T_d: 303 °C. <sup>1</sup>H NMR (500 MHz, d6-DMSO): No peak. <sup>13</sup>C NMR (500 MHz, d6-DMSO): <math display="inline">\delta$  163.42, 160.68, 158.23, 141.37 ppm. IR (KBr):  $\upsilon$  3508, 3367, 1677, 1593, 1519, 1499, 1435, 1344, 1312, 1178, 1138, 1042, 970, 916, 875, 823, 714 cm<sup>-1</sup>. Elemental analysis for C\_8Na\_2N\_{12}O\_8 (438.14): calcd C 21.93, N 38.36%. Found: C 21.78, N 38.48%.

### **Conflicts of interest**

There are no conflicts to declare.

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# Nitramino-functionalized tetracyclic oxadiazoles Nonplanar G Mechanical sensitivity Tetracyclic backbone S safer explosives S afer explosives Detonation performance Dihydroxylammonium salt D: 9030 m/s P: 36.0 GPa

The combination of 1,2,4-oxadiazole and nitramino-1,2,5-oxadiazole is a promising strategy for designing energetic materials with high performance and high stability.