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In this work, a series of new compounds **2-9** was synthesized through a simple, safe and efficient route. Dihydroxyiminomalonic acid diamide was chosen as the starting material to react with trichloroacetic anhydride to form 1,2,4-oxadiazole rings. Then the products from the ring-forming reaction reacted with an excess amount of ammonia in methanol to give 3,3'-methylenebis(1,2,4-oxadiazol-5-amine) (**2**). Further nitration of compound **2** gave *N*,*N*'-(methylenebis(1,2,4oxadiazole-3,5-diyl))dinitramide (**3**, DNAMBO). A serial of DNAMBO-based energetic salts **4-9** pairing with nitrogen-rich cations were readily obtained by treating compound **3** with two equivalents of free bases. The physicochemical and energetic properties of compounds **3-9**, including density, thermal stability, and sensitivity, were investigated, as well as the detonation performances were calculated by the Kamlet-Jacobs equations. Among them, the hydrazinium salt (**5**) shows the best detonation performances (**5**: *d*=1.69 g cm⁻³; *T*_d=147.5 °C; *P*=27.1 GPa; v_D=7962 m s⁻¹).

Introduction

In the development of new energetic materials, high energy, high stability, and green synthesis have always been among our most sought after goals^[1]. Taking the nitrogen-oxygen heterocycle as the skeleton and introducing explosophores such as nitro and nitramino group are one of the main ideas for constructing energetic compounds in recent years. It is undeniable that, guided by this idea, a large number of new energetic compounds with excellent properties have been synthesized^[2]. However, we should also note at the same time that there are some problems in the synthesis of these energetic molecules, for example, the synthetic route is two long, the raw materials are not readily available or safe enough to use, which will make it very difficult for scale-up and further application.

Nitramino-1,2,4-oxadiazole has been intensively used as a block with high energy and good stability in the construction of several new energetic compounds^[3], e.g. the hydroxylammonium salts of N-(4-(5-(nitroamino)-1,2,4-oxadiazol-3-yl)-1,2,5-oxadiazol-3-yl)nitramide (**a**)^[4], N,N'-([3,3'-bi(1,2,4-oxadiazole)]-5,5'-diyl)dinitramide (**b**)^[5] and 4-(5-(nitroamino)-1,2,4-oxadiazol-3-yl)-3-(1H-tetrazol-5-yl)-1,2,5-

oxadiazole-2-oxide (c)^[6] (scheme 1). These reported energetic salts show good comprehensive performances (scheme 1).



Scheme 1 Selected energetic materials based on 1,2,4-oxadiazole ring.

In the reports of these documents, the construction of amino-1,2,4-oxadiazole, the precursor of nitramino-1,2,4-oxadiazole, exclusively proceed by the reaction between amino-oxime and cyanogen bromide (Route 1 in scheme 2). Due to the high toxicity and sublimation characteristics of cyanogen bromide, there are huge potential safety hazards in its use. In addition, it was found that the synthesis of some compounds containing amino-1,2,4-oxadiazole block through Route 1 was unsuccessful in our previous work. Based on these considerations, we referred to the literature^[7] and selected a safer and more efficient route (Route 2 in scheme 2) to construct some new compounds containing amino-1,2,4-oxadiazole block.

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In this study, we bridged two nitramino-1,2,4-oxadiazole blocks with methylene, a non-energetic fragment, and hoped to build a new energetic compound with low low sensitivity. In order to construct the nitration precursor (3.3'and methylenebis(1,2,4-oxadiazol-5-amine) (2)) safely efficiently, we chose dihydroxyimino-malonic acid diamide as the starting material and it reacted with trichloroacetic anhydride to form 1,2,4-oxadiazole rings. Then the obtained compound 1 reacted with an excess amount of ammonia in methanol to give compound 2. After nitration of compound 2, synthesized N,N'-(methylenebis(1,2,4we successfully oxadiazole-3,5-diyl))dinitramide (3). In order to synthesize energetic materials with higher detonation performances, we tried to introduce nitro group onto the methylene group of compound 2, but failed to get the target compound 10. All new compounds in this work were fully characterized and a series of physical and chemical properties of these energetic compounds were investigated in detail.

Results and Discussion

Synthesis

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59 60 Dihydroxyimino-malonic acid diamide was chosen as the starting material to react with trichloroacetic anhydride at 140 °C to give bis(5-(trichloromethyl)-1,2,4-oxadiazol-3-yl)methane (1) in the yield of 91.5 %. The ammonolysis of 1 took place when an excess amount of gaseous ammonia was bubbled into the solution of 1 in methanol, and compound 2 precipitated from the reaction mixture after stirring overnight. We also tried to get compound 2 by treating dihydroxyimino-malonic acid diamide with cyanogen bromide in methanol, but failed to separate valuable products.

Initially, we tried to nitrate compound **2** directly by using 100% nitric acid and found that it was difficult to extract the product with various solvents after quenching the reaction mixture with water. The reason behind this might be that the product is quite soluble in water. Therefore we chose the widely used N₂O₅ as the nitration agent because the remaining N₂O₅ can easily be removed. When the nitration reaction in N₂O₅/CHCl₃ system was complete, compound **3** was obtained as high purity solid by simplify removing N₂O₅ and CHCl₃ under vacuum and washing the crude products with a small amount of methanol.

Compounds **4-9**, a series of energetic salts of <u>compound</u>, were prepared by treating the solution of <u>compound</u> are ethanol with different free bases and the products precipitated from the reaction mixture and were collected by filtration. These energetic salts were fully characterized by NMR (¹H, ¹³C), IR and elemental analysis, and salt **4** was further confirmed by single-crystal X-ray diffraction.

In order to synthesize energetic materials with higher detonation performances, we tried to introduce nitro group on the methylene group of compound **2** by treating it with mixed acid (fuming nitric acid/98% sulfuric acid, and fuming nitric acid/trifluoroacetic anhydride), but failed to get the target compound **10**.



Scheme 3 Synthetic route of compounds 1-10

NMR spectroscopy

All NMR (¹H, ¹³C) data were recorded for compounds **1-9** in DMSO- d_6 solution. For compound **2**, the position of the resonance bands for the proton of methylene was observed at 3.67 ppm, and those for amino groups were recorded at 7.74 ppm. Compared to compound **2**, the signal of acidic protons of compound **3** are downshifted to 9.20 ppm in the ¹H NMR owing to the powerful electron-withdrawing effect of the nitro group, the position of the resonance band for the proton of methylene are shifted to 4.24 ppm at the same time. Since the deprotonation of **4** with nitrogen-rich bases, the ¹H NMR signal of proton on methylene were observed from 3.82 to 3.88 ppm for compounds **4-8** and the signal of corresponding cations were also recorded in the ¹H NMR.

In the ¹³C NMR, the signal of oxadiazole rings in compound **2** were observed at 170.0 and 163.4 ppm, the signal of the methylene group in compound **2** was at 23.7 ppm. All the ¹³C NMR signals of compound **3** are shifted to the higher field compared with compound **2**. This phenomenon is somewhat abnormal. In general, after the amino group on the oxadiazole ring is nitrated, the ¹³C NMR signal of the carbon directly connected to the nitramino group will move to the lower field due to the strong electron-withdrawing effect of the nitramino

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group. For the ionic derivatives (salts **4-9**) of **3**, deprotonation of **3** resulted in a downshifting (salt **4**: 175.25, 165.94, 24.66 ppm *vs* **3**: 170.26, 159.65, 22.15 ppm).

X-ray crystallography

X-ray quality crystals of **4** was obtained by evaporation of its aqueous solution. It crystallized in the monoclinic space group with C 2/c symmetry, and has four units in the unit cell (Z=4). Its crystal density is 1.738 g cm⁻³ at 296 K. It can be seen from the torsion angles of -179.07° (C2-N2-C1-C3), 175.41° (N2-C1-C3-C1), 6.27° (C2-N3-N4-O2) and -177.12° (N1-O1-C2-N3) that all atoms of the entire anion are almost coplanar and two cations are trapped between the DNAMBO anion planes. The single-crystal X-ray structure and unit cell view of **4** along b axis are shown in Figure 1.







Thermal stabilities

Thermal decomposition temperature is an important indicator for evaluating the thermal stability of an energetic material. Energetic material with good thermal stability will greatly improve their safety during production and use^[8]. Generally speaking, the decomposition temperature of a useful energetic material tends to be higher than 150 °C^[9]. In this work, the series of newly prepared compounds **3-8** have acceptable thermal stability with decomposition temperatures being between 148 °C and 209 °C. As shown in Figure 2, compound **3** decompose at 152 °C and loses crystal water at 122 °C, which corresponded to a weight loss on the TG curve.

All energetic salts with the exception of **5** are more thermally stable than compound **3**, and their thermal decomposition temperatures range from 183 (**8**) to 209 °C (**4**). Unexpectedly, salt **5** shows a comparatively low decomposition temperature of 148 °C, which is even lower than that of compound **3** (152 °C).



Figure 2 DSC curves of compounds 3-10 at a heating rate of 5 K min⁻¹

Densities

According to the Kamlet-Jacobs equations, we know that density is one of the main factors determining the detonation performance of energetic materials^[10-11].

The densities of compounds **3-9** were measured by using a gas pycnometer at room temperature and the results are listed in Table 1. The measured densities of compounds **3-9** are distributed between 1.763 g cm⁻³ (**4**) and 1.568 g cm⁻³ (**6**). Among them, compound **4** possesses the highest density of 1.763 cm⁻³. Except for compounds **6** (1.568 g cm⁻³) and **7** (1.612 g cm⁻³), all of these compounds have a higher density than TNT (1.65 g cm⁻³).

Sensitivities

For initial safety testing, the sensitivities of the newly prepared compounds **3-8** towards friction and impact were measured by using BAM drop hammer (BFH-10) and BAM friction tester (FSKM-10) and the results are listed in Table 1.

A large number of studies have shown that the impact sensitivity of energetic materials are closely related to their electrostatic potential (ESP)^[12-14]. In most N-O systems, such as nitro (–NO₂) and nitramine (–NH–NO₂), the regions of stronger positive potential accumulated around the nitrogen atoms will result in an abnormal imbalance, which in theory will cause the high impact sensitivity^[15]. In order to understand this relationship more intuitively, we calculated the ESP of compound 3 using Gaussian 09 at the theoretical level of B3LYP/6-31+g(d,p) before the actual measurement of the sensitivity. As can be seen from the calculated EPS image of compound **3** showed in Figure 3, the positive potential on the ring is more uniformly dispersed, while the nitrogen atom of the nitro group accumulates positive potential, so we suspect that the impact sensitivity of compound 3 may be relatively high, which was confirmed experimentally.

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Figure 3 Electrostatic potential of compound 3 [B3LYP/6-311+g- (2d,p), 0.001 electron/b3 isosurface, energy values -0.06 to +0.06 H]. Color coding: yellow, slightly negative; green, neutral; turquoise, slightly positive; light blue, positive; dark blue, very positive.

Impact sensitivities and friction sensitivities of compounds 3-8 are in the range of 3 J (5) to 14 J (9) and 96 N (5) to >360 N (6), respectively. Among these compounds, the impact and friction sensitivity of compound **3** are not particularly satisfactory, at 5 J and 160 N respectively. Salt 6 has the lowest friction sensitivity (> 360 N) and good impact sensitivity (12 J). And the results are listed in Table 1.

Heats of formation

Heat of formation is an important parameter in evaluating the detonation performance of energetic materials. All calculations were accomplished by using the Gaussian 09 (Revision A.01) suite of programs^[16]. The geometric optimization of the structures and frequency analyses were carried out by using the B3LYP functional with the 6-31+G**basis set, and single-point energies were calculated at the MP2(full)/6-311++G**level. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. The remaining task, the heats of formation of compound 3 and its corresponding anion, were calculated by employing the isodesmic reaction approach.



According to the Born-Haber energy cycle, the relationship between the $\Delta H_{\rm f}$ values of the cations and anion of the cations and anion of the cation of t can be expressed by the following equation.

 $\Delta H_{f^{\circ}}(\text{ionic salt, 298K}) = \Delta H_{f^{\circ}}(\text{cation, 298K}) + \Delta H_{f^{\circ}}(\text{anion, 298K})$ $-\Delta H_{L}$ (1)

The ΔH_L value could be predicted by the formula suggested by Jenkins et al [Eq. (2)]^[17], where U_{POT} is the lattice potential energy and nM and nX depend on the nature of the ions M^p + and X^q ⁻, respectively, and are equal to three for monoatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions.

$$\Delta H_{\rm L} = U_{\rm POT} + [p(n_{\rm M}/2-2) + q(n_{\rm X}/2-2)]RT$$
⁽²⁾

The equation for the lattice potential energy, $U_{\rm POT}$, takes the form of Equation (3), where $\rho_{\rm m}$ is the density (g cm⁻³), Mm is the chemical formula mass of the ionic material (g), and the coefficients v (kJ⁻¹mol⁻¹cm) and δ (kJ⁻¹mol⁻¹) are assigned literature values.





As shown in Table 1, the $\Delta H_{\rm f}$ values of compounds **3-9** were calculated to be in the range of -39.1 to 429.3 kJ mol⁻¹. Among them, the $\Delta H_{\rm f}$ value of compound **3** were calculated to be 115.9 kJ mol⁻¹ and diaminoguanidinium salt (8) possesses the highest $\Delta H_{\rm f}$ value of 429.3 kJ mol⁻¹.

Detonation performances

Detonation velocity $(v_{\rm D})$ and detonation pressure (P) are two basic parameters for evaluating the detonation performance of energetic materials. With calculated heats of formation and measured densities, we calculated the detonation velocities and detonation pressures of compounds 3-8 according to the Kamlet-Jacobs equations^[11]. According to the calculation results, we can see that their detonation velocities are distributed in the range of 6845 m s⁻¹ to 7962 m s⁻¹, and their detonation pressures are distributed in the range of 19.1 GPa to 27.1 GPa. Although the measured density of 5 is relatively low, it has the best detonation performance ($v_{\rm D}$ =7962 m s⁻¹, P=27.1 GPa) due to its high heat of formation.

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Compd	$T_{d}^{[a]}$	d ^[b]	$\Delta_{\rm f} H_{\rm L}^{\rm [c]}$	$\Delta_{\rm f} H_{\rm cation}^{\rm [d]}$	$\Delta_{\rm f} H_{\rm anion}^{\rm [e]}$	$\Delta_{\rm f} H_{\rm salt}^{\rm [f]}$	$P^{[g]}$	$V_D^{[h]}$	IS ^[i]	FS ^[j]	OB ^[k]
3	152	1.744	-	-	-	115.9	26.4	7787	5	160	-35.3
4	209	1.763	1328.8	635.8	18.1	-39.1	26.5	7775	8	324	-46.9
5	148	1.694	1265.8	774.1	18.1	300.5	27.1	7962	3	96	-47.6
6	195	1.568	1160.3	563.7	18.1	-14.8	19.1	6845	11	>360	-61.5
7	199	1.612	1139.8	660.3	18.1	198.9	23.4	7511	9	192	-60.9
8	183	1.676	1126.8	769	18.1	429.3	24.9	7661	7.5	128	-60.4
9	192	1.728	1121.0	804.5	18.1	389.1	23.0	7291	14	168	-64.6
TNT	295	1.65	-	-	-	-59.4	21.3	7303	15	353	-74.0

[a] Decomposition temperature (onset) [°C] [b] Density measured by gas pycnometer at 25°C [g cm⁻³]. [c] Calculated molar lattice energy [kJ mol⁻¹] [d] molar enthalpy of formation of cation [kJ mol⁻¹] [e] Calculated molar enthalpy of formation of anion [kJ mol⁻¹] [f] Calculated molar enthalpy of formation of salts [kJ mol⁻¹] [g] Detonation pressure [GPa] [h] Detonation velocity [m s⁻¹] [i] Impact sensitivity [J] [j] Friction sensitivity [N] [k] Oxygen balance (OB) is an index of the deficiency or excess of oxygen in a compound required to convert all C into CO₂ and all H into H₂O, for the compound with the molecular formula of C_aH_bN_cO_d, OB(%)=1600[(d-2a-b/2)/Mw] [%].

Experimental Section

General methods: The ¹H and ¹³C spectra were recorded on a 400 MHz nuclear magnetic resonance spectrometer operating at 400 and 100 MHz and chemical shifts are reported relative to tetramethylsilane. The solvent was [D₆]dimethyl sulfoxide ([D₆]DMSO) unless otherwise specified. The melting and decomposition points were recorded on a NETZSCH STA 449F3 equipment at a heating rate of 5°C min⁻¹, respectively. Infrared spectra were recorded by using KBr pellets. Densities for compounds **3-9** were measured at room temperature using a Micromeritics Accupyc II 1340 gas pycnometer. Elemental analyses were obtained on an Elementar Vario MICRO CUBE (Germany) elemental analyzer.

X-ray crystallography: Crystals of salt 4 were removed from the flask and covered with a layer of hydrocarbon oil, respectively. A suitable crystal was selected, attached to a glass fiber, and placed in the low-temperature nitrogen stream. The singlecrystal X-ray diffraction data were collected at 173 K using a Bruker CCD area detector diffractometer equipped with a graphite-monochromatized MoK α radiation (λ =0.71073 Å) using omega scans. Data collection and reduction were performed and the unit cell was initially refined by using Bruker SMART software. The reflection data were also corrected for Lp factors. The structure was solved by direct methods and refined by least squares method on F² using Bruker SHELXTL program. Structure was solved in the space group P-1 by analysis of systematic absences. In this all-lightatom structure the value of the Flack parameter did not allow the direction of polar axis to be determined and Friedel reflections were then merged for the final refinement. Details of the data collection and refinement are given in Table S1.

CCDC-1877493 (4) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Dihydroxyimino-malonic acid diamide

Malononitrile (5 g, 75.96 mmol) was dispersed in water (40 mL). Hydroxylamine aqueous solution (50%, 10 mL, 151.37 mmol) was added to the above system at room temperature. After stirring overnight, the precipitate was filtered and washed with ice water, dried in air to give dihydroxyiminomalonic acid diamide (9.5 g, yield 95%). ¹H NMR (400 MHz, DMSO-d₆): 4.42 (s, 2H) ppm; ¹³C NMR (400MHz, DMSO-d₆): 175.32, 166.02, 83.15, 24.49 ppm.

Bis(5-(trichloromethyl)-1,2,4-oxadiazol-3-yl)methane (1)

Dihydroxyimino-malonic acid diamide (5 g, 37.84 mmol) was dispersed in trichloroacetic anhydride (28 mL, 151.37 mmol) at room temperature. Then, the mixture was heated to 105 °C and reacted for 3.5 h. After cooled down to RT, the reaction mixture was poured into ice water (150 mL) and stirred for 0.5 h. The precipitate was filtered and washed with ice water to give **1** (13.2 g, yield 92%). ¹H NMR (400 MHz, DMSO-d₆): 9.01 (s, 2H), 5.33 (s, 4H), 2.68 (s, 2H) ppm; ¹³C NMR (400MHz, DMSO-d₆): 149.68, 33.40 ppm.

3,3'-Methylenebis(1,2,4-oxadiazol-5-amine) (2)

Compound **1** (13.2 g, 34.4 mmol) was dispersed in methanol (20 mL) at 5 °C, and excess gaseous ammonia was bubbled into the methanol solution for 40 min. A large amount of white solid precipitated from the reaction mixture and was collected by filtration followed by washing with methanol and drying in air to give compound **2** (4.57 g, yield 73%). ¹H NMR (400 MHz,

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DMSO-d₆): 7.74 (s, 4H), 3.67 (s, 2H) ppm; ¹³C NMR (400MHz, DMSO-d₆): 172.02, 166.34, 23.74 ppm.

$\textit{N,N}'-(Methylenebis(1,2,4-oxadiazole-3,5-diyl))dinitramide (3 \cdot H_2O)$

Compound **2** (1.4 g, 7.7 mmol) was dispersed in a solution of N_2O_5 (9 g, 7.69 mmol) in chloroform (50 mL) under an icewater bath. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. After removing the solvent and N_2O_5 under vacuum, methanol (5 mL) was added and the mixture was stirred for 10 min to give a white precipitate, which was then filtered and washed with methanol to give compound **3** (1.5 g, yield 71%). FI-IR (KBr pellet, cm⁻¹): 3581, 3485, 3238, 2967, 2231, 2085, 2046, 1933, 1616, 1506, 1456, 1276, 1174, 1068, 1004, 968, 899, 845, 792, 779, 758, 728, 666, 625, 615, 504, 468, 429, 418. ¹H NMR (400 MHz, DMSO-d₆): 9.20 (s, 2H), 4.24 (s, 2H) ppm; ¹³C NMR (400MHz, DMSO-d₆): 170.26, 159.65, 22.15 ppm; Anal. Calcd. For $C_5H_4N_8O_6$: C 20.70, H 2.08, N 38.62; found: C 20.78, H 2.02, N 38.73.)

Diammonium *N*,*N*'-(methylenebis(1,2,4-oxadiazole-3,5-diyl)) dinitramide (4)

Compound **3** (200 mg, 0.734 mmol) was dispersed in ethanol (1.5 mL), and gaseous ammonia was bubbled into the system until its pH value was higher than 7. After stirring at room temperature for 3 h, the precipitate was filtered, washed with a small amount of ethanol and dried in air to give **4** (174 mg, yield 77%). FI-IR (KBr pellet, cm⁻¹): 3193, 2251, 1982, 1543, 1444, 1393, 1262, 1211, 1094, 988, 926, 777, 763, 753, 741, 724, 621, 478, 411; ¹H NMR (400 MHz, DMSO-d₆): 6.98 (s, 8H), 3.87 (s, 2H) ppm; ¹³C NMR (400MHz, DMSO-d₆): 175.25, 165.94, 24.66 ppm; Anal. Calcd. For C₅H₁₀N₁₀O₆: C 19.61, H 3.29, N 45.74; found: C 19.59, H 3.33, N 45.99.

General procedures for the preparation of salts 5 and 9.

Compound **3** (200 mg, 0.734 mmol) was dispersed in ethanol (1.5 mL) at room temperature followed by adding two equivalents of free base (hydrazine hydrate (80%) or 3,5-diamino-1,2,4-triazole) in one portion. After stirring at room temperature for 3 h, the precipitate was filtered, washed with a small amount of ethanol and dried in air to give the desired product.

Dihydrazinium N,N'-(methylenebis(1,2,4-oxadiazole-3,5-diyl)) dinitramide (5)

White powder; Yield: 198 mg, 80%; FI-IR (KBr pellet, cm⁻¹): 3342, 3242, 2989, 2007, 1594, 1559, 1513, 1404, 1362, 1313, 1262, 1182, 1088, 1000, 950, 869, 841, 776, 752, 739, 620, 479, 444; ¹H NMR (400 MHz, DMSO-d₆): 8.44 (s, 10H), 3.88 (s, 2H) ppm; ¹³C NMR (400MHz, DMSO-d₆): 174.93, 165.66, 24.35 ppm; Anal. Calcd. For $C_5H_{12}N_{12}O_6$: C 17.86, H 3.60, N 49.99; found: C 17.82, H 3.61, N 50.02.

Bis(3,5-diamino-1,2,4-triazolium) N,N'-(methylenebis(1,2,4oxadiazole-3,5-diyl))dinitramide (9)

White powder; Yield: 306 mg, 89%; FI-IR (KBr pellet, cm⁻¹): 3625, 3410, 3262, 3175, 2872, 2809, 2651, 1697, 1670, 1525, 1511, 1455, 1399, 1343, 1418, 1319, 1288, 1261, 1171, 1108, 1061, 1009, 984, 929, 846, 816, 797, 760, 735, 693, 663, 623, 497; ¹H NMR (400 MHz, DMSO-d₆): 7.05^D(s): 124H); 93.82 (s) 2H) ppm; ¹³C NMR (400MHz, DMSO-d₆): 174.83, 165.82, 159.73, 24.50 ppm; Anal. Calcd. For C₉H₁₄N₁₈O₆: C 22.98, H 3.00, N 53.61; found: C 22.52, H 3.06, N 52.13.

Bis(guanidinium) N,N'-(methylenebis(1,2,4-oxadiazole-3,5diyl))dinitramide (6)

One equivalent of guanidine carbonate (132 mg, 0.734 mmol) was added into the solution of **3** (200 mg, 0.734 mmol) in ethanol at room temperature. After stirring at room temperature until no further gas evolution, the precipitate was filtered, washed with a small amount of ethanol and dried in air to give **6** (248 mg, yield 86%). FI-IR (KBr pellet, cm-1): 3178, 2804, 2292, 2010, 1651, 1538, 1428, 1300, 1211, 1086, 1030, 1011, 997, 972, 949, 937, 915, 871, 828, 842, 773, 741, 633, 543; ¹H NMR (400 MHz, DMSO-d6): 6.93 (s, 12H), 3.82 (s, 2H) ppm; ¹³C NMR (400MHz, DMSO-d6): 174.75, 165.78, 24.46 ppm; Anal. Calcd. For $C_7H_{14}N_{14}O_6$: C 21.54, H 3.62, N 50.25; found: C 21.39, H 3.63, N 50.17.

Bis(aminoguanidinium) *N,N*'-(methylenebis(1,2,4-oxadiazole-3,5diyl))dinitramide (7)

Tow equivalents of aminoguanidine bicarbonate (200 mg, 1.47 mmol) were added into the solution of **3** (200mg, 0.734mmol) in ethanol at room temperature. After stirring at room temperature until no further gas evolution, the precipitate was filtered, washed with a small amount of ethanol to give **7** (298mg, yield 96%) after drying in air. FI-IR (KBr pellet, cm⁻¹): 3449, 3347, 3296, 2990, 2949, 1671, 1655, 1559, 1543, 1511, 1432, 1404, 1313, 1262, 1181, 1089, 987, 966, 841, 827, 781, 750, 740, 726, 664, 654, 610, 477; ¹H NMR (400 MHz, DMSO-d₆): 8.62 (s, 2H), 7.25 6.80 (d, 8H), 4.68 (s, 4H), 3.83 (s, 2H) ppm; ¹³C NMR (400MHz, DMSO-d₆): 174.79, 165.84, 158.83, 24.50 ppm; Anal. Calcd. For C₇H₁₆N₁₆O₆: C 20.00, H 3.84, N 53.32; found: C 19.85, H 4.08, N 52.71.

Bis(diaminoguanidinium) *N*,*N*'-(methylenebis(1,2,4-oxadiazole-3,5-diyl))dinitramide (8)

N,N'-Diaminoguanidine hydrochloride (185 mg, 1.47 mmol) was neutralized with equal molar solution of NaOH (40 mg, 1.0 mmol) in ethanol (2 mL). After stirring at room temperature for 30 min, the filtrate A was obtained by filtration. **3** (200 mg, 0.734 mmol) was dispersed in the filtrate A and stirred for 3 h. The precipitate was collected by filtration and washed with ethanol to give the product **8** (208 mg, yield 63%) after air drying. FI-IR (KBr pellet, cm⁻¹): 3419, 3268, 3087, 2992, 2892, 2292, 2005, 1682, 1542, 1436, 1378, 1358, 1272, 1180, 1085, 1032, 996, 970, 932, 910, 870, 779, 765, 753, 744, 725, 655, 642, 547, 477, 426; ¹H NMR (400 MHz, DMSO-d₆): 8.57 (s, 4H), 7.14 (s, 4H), 4.59 (s, 8H), 3.82 (s, 2H) ppm; ¹³C NMR (400MHz, DMSO-d₆): 174.83, 165.82, 159.73, 24.50 ppm; Anal. Calcd. For C₇H₁₈N₁₈O₆: C 18.67, H 4.03, N 55.99; found: C 19.16, H 4.03, N 54.32.

Conclusions

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In this work, a series of new energetic compounds 2-9 were synthesized through a simple, safe and efficient route. N,N'-(Methylenebis(1,2,4-oxadiazole-3,5-diyl))dinitramide (3) and its energetic salts (4-9) were fully characterized by multinuclear NMR (¹H, ¹³C), IR spectroscopy and elemental analysis, and salt 4 was further confirmed by single-crystal Xray diffraction. Except for salt 5, salts 4-9 show excellent thermal stabilities of 183 (8) to 209 °C (4), which are much better than their parent compound **3** (T_d =152 °C). Their densities were measured to be in the range of 1.568 g cm^{-3} (6) and 1.763 g cm⁻³ (4). Among them, the diammonium salt (4) shows the highest density (d=1.763 g cm⁻³). Their impact sensitivities and friction sensitivities were determined to be in the range of 3 J (5) and 14 J (9) and 96 N (5) to >360 N (6), respectively. And their detonation pressures and detonation velocities were calculated according to Kamlet-Jacobs equations to be between 19.1 (6) and 27.1 (5) GPa and 6845 (6) and 7962 (5) m s⁻¹, respectively. Among them, the dihydrazinium salt (5) shows the best detonation performance performances (5: *P*=27.1 GPa; *v*_D=7962 m s⁻¹).

Conflicts of interest

The authors declare no conflict of interest.

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