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Synthesis of Energetic Salts Based on 5,5'-Dinitroamino-2,2'-bi(1,3,4-oxadiazole)

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Abstract: Using 5,5'-dinitroamino-2,2'-bi(1,3,4-oxadiazole) as starting material, a series of energetic salts were synthesized. All compounds were characterized by FT-IR, multinuclear NMR spectroscopy and elemental analysis. The structures of di(3-amino-1,2,4-triazolium) 5,5'-dinitroamino-2,2'-bi(1,3,4-oxadiazolate)·2H₂O (**9**·2H₂O) and di(4-amino-1,2,4-triazolium) 5,5'-dinitroamino-2,2'-bi(1,3,4-oxadiazolate) (**10**) were further confirmed by single crystal X-ray diffraction. Their thermal stabilities were determined by differential scanning calorimetry (DSC). The detonation performance was calculated with Explo5 v6.02 software. The results show that the temperature of the thermal decomposition reaction is in the range of 146.8–239.9 °C. The calculated detonation velocity and pressure are higher than 7693 m·s⁻¹ and 21.3 GPa, respectively. Their densities are from 1.683 to 1.941 g·cm⁻³. The measured impact sensitivities are between 10 J and 28 J and friction sensitivities are between 160 N and 360 N, which indicated that most salts of 5,5'-dinitroamino-2,2'-bi(1,3,4-oxadiazole) are high energy-density materials with good properties.

Key words: energetic materials; 1,3,4-oxadiazole; X-ray diffraction; sensitivity; explosive performance

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1 Introduction

Over the past decade, the synthesis and development of new high-energy density materials (HEDMs) have attracted increasing attention in the world^[1-2]. New HEDMs not only focus on high density, high detonation velocity and pressure but also aim at the high positive heat of formation, high thermal stability, low sensitivity towards external forces such as impact and friction and environmental compatibility. However, among these characteristics, high performance and low sensitivity tend to be contradicting aspects, making the design and synthesis of energetic

materials an interesting and challenging work^[3-4]. Heterocyclic energetic salts with high nitrogen content is one of the favorite topics in the search for high-performance energetic materials recently^[5-8]. The energetic salts possess advantages over nonionic molecules since these salts tend to exhibit lower vapor pressures and higher thermal stability than their atomically similar nonionic analogues. This provides an efficient methodology for the design and synthesis of HEDMs^[9-10].

Oxadiazole is a favorite example of a nitrogen- and oxygen-rich ring that has been widely used in the syntheses of drugs, ionic liquids and scintillators. The energetic materials based on 1,2,5-oxadiazole (furan) have been exhaustively investigated^[11-14]. Compared to furan, 1,3,4-oxadiazoles have been studied very rarely as energetic materials. The energetic materials based on 1,3,4-oxadiazole have become more and more attractive due to their higher thermal stability and lower sensitivity^[15-16]. For example, di(4-amino-1,2,4-triazolium) 5,5'-dinitromethyl-2,2'-bis(1,3,4-oxadiazolate)

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(**A**)^[17] shows a detonation velocity of 8601 m · s⁻¹ and a detonation pressure of 31.8 GPa; hydrazinium 2,5-bis(trinitromethyl)-1,3,4-oxadiazolate (**B**)^[16], has a high density of 1.90 g · cm⁻³ and excellent detonation performance ($D=8900$ m · s⁻¹, $p=36.3$ GPa). And both of them have good thermal stabilities (**A**: 205.8 °C; **B**: 190 °C) and acceptable sensitivity towards impact and friction (**A**: IS: 16 J, FS: 200 N; **B**: IS: 19 J, FS: 80 N).

In our effort to seek more powerful, eco-friendly and less sensitive explosives, we were interested in 5,5'-dinitroamino-2,2'-bi(1,3,4-oxadiazole), because of its high thermal stability (decomposition temperature 210 °C), high density (1.99 g · cm⁻³) and excellent explosive properties ($D=9481$ m · s⁻¹, $p=41.9$ GPa)^[18-20]. However, energetic salts based on 5,5'-dinitroamino-2,2'-bi(1,3,4-oxadiazole) have not been fully investigated. Herein, we report the synthesis and characterization of energetic salts based on 5,5'-dinitroamino-2,2'-bi(1,3,4-oxadiazole). All the salts are well characterized by IR and multinuclear NMR spectroscopy, differential scanning calorimetry (DSC) and elemental analysis, and some are further measured by single crystal X-ray diffraction. Their key detonation performance and sensitivity towards impact and friction were determined by experimental and theoretical methods.

2 Experiments

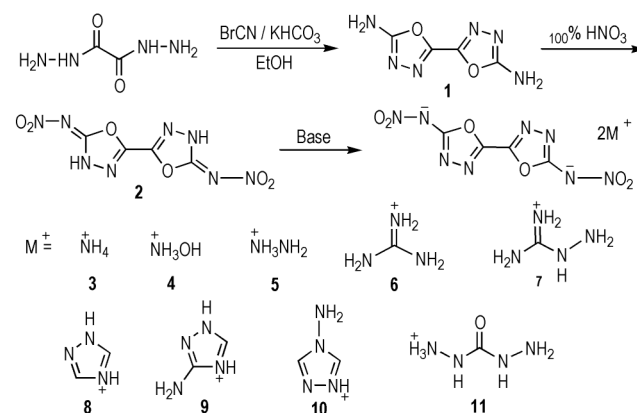
2.1 General Methods

¹H and ¹³C spectra were recorded on a 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer operating at 500 and 125 MHz. The chemical shifts were given relative to external tetramethylsilane. IR spectra were recorded by using the attenuated total reflection mode for solids on a Thermo Scientific Nicolet is 10 spectrometer. The decomposition temperatures were determined on a differential scanning calorimeter (DSC823e instrument) at a heating rate of 5 °C · min⁻¹. Elemental analysis was performed with a Vario EL III instrument. Sensitivity towards impact and friction was determined using

an HGZ-1 drop hammer and a BAM friction tester. The densities of the compounds were determined at room temperature by employing a gas pycnometer.

2.2 Synthetic Route

Synthesis of energetic salts based on 5,5'-dinitroamino-2,2'-bi(1,3,4-oxadiazole) are shown in Scheme 1.



Scheme 1 Synthesis of energetic salts based on 5,5'-dinitroamino-2,2'-bi(1,3,4-oxadiazole)

The starting material 5,5'-diamino-2,2'-bi(1,3,4-oxadiazole) (**1**) was prepared by treating oxalyl dihydrazide with cyanogen bromide in anhydrous ethanol for 24 h. Nitramino substituted compound **2** was obtained by direct nitration of 5,5'-diamino-2,2'-bi(1,3,4-oxadiazole) using 100% nitric acid at 0 °C. The energetic salt derivatives of compound **2** were readily synthesized by the acid-base neutralization reaction in which compound **2** reacted with such as ammonia, hydroxylamine, hydrazine, guanidine, aminoguanidine, 1,2,4-triazole, 3-amino-1,2,4-triazole, 4-amino-1,2,4-triazole and carbohydrazide.

General procedures for compounds **3-11**: NH₃ · H₂O (2.0 mmol), hydroxylamine solution (2.0 mmol), hydrazine hydrate (2.0 mmol), guanidine carbonate (1.0 mmol), aminoguanidine bicarbonate (2.0 mmol), 1,2,4-triazole (2.0 mmol), 3-amino-1,2,4-triazole (2.0 mmol) and 4-amino-1,2,4-triazole (2.0 mmol), carbohydrazide (2.0 mmol) were, respectively, added to a solution of compound **2** (0.258 g, 1.0 mmol) in 30 mL of acetonitrile and the mixture was stirred at room temperature. After 2 h the

precipitate was filtered, washed with ether and air-dried to yield.

2.3 Characterization

Ammonium 5, 5'-dinitroamino-2, 2'-bi(1, 3, 4-oxadiazolate)(3)

$\text{NH}_3 \cdot \text{H}_2\text{O}$ (2.0 mmol) was added to a solution of compound **2** (0.258 g, 1.0 mmol) in 30 mL of acetonitrile and the mixture was stirred at room temperature. After 2 h the precipitate was filtered, washed with ether and air-dried to yield. 0.237 g of compound **3** was obtained as a yellow solid in a yield of 81.1%. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 7.17 (s, 8H). ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ : 166.15 (s), 148.32 (s). IR (KBr, ν/cm^{-1}): 3448, 3372, 3216, 3050, 1524, 1488, 1447, 1424, 1430, 1311, 1279, 1150, 1069, 1022, 963, 728. Anal. calcd for (%) for $\text{C}_4\text{H}_8\text{N}_{10}\text{O}_6$ (292.17): C 16.44, H 2.76, N 47.94; found: C 16.52, H 2.53, N 47.52.

Hydroxylammonium 5,5'-dinitroamino-2,2'-bi(1,3,4-oxadiazolate)(4)

Hydroxylamine solution (2.0 mmol) was added to a solution of compound **2** (0.258 g, 1.0 mmol) in 30 mL of acetonitrile and the mixture was stirred at room temperature. After 2 h the precipitate was filtered, washed with ether and air-dried to yield. 0.279 g of compound **4** was obtained as a yellow solid in a yield of 86.1%. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 7.09. ^{13}C NMR (125 MHz, D_2O) δ : 167.41 (s), 149.97 (s). IR (KBr, ν/cm^{-1}): 3448, 3138, 2718, 1582, 1523, 1489, 1417, 1339, 1289, 1159, 1078, 1017, 987, 775, 728. Anal. calcd for (%) for $\text{C}_4\text{H}_8\text{N}_{10}\text{O}_8$ (324.17): C 14.82, H 2.49, N 43.21; found C 14.71, H 2.38, N 43.33.

Hydrazinium 5, 5'-dinitroamino-2, 2'-bi(1, 3, 4-oxadiazolate)(5)

Hydrazine hydrate (2.0 mmol) was added to a solution of compound **2** (0.258 g, 1.0 mmol) in 30 mL of acetonitrile and the mixture was stirred at room temperature. After 2 h the precipitate was filtered, washed with ether and air-dried to yield. 0.254 g of compound **5** was obtained as a yellow solid in a yield of 78.9%. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 6.16 (br.). ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ : 166.11

(s), 148.34 (s). IR (KBr, ν/cm^{-1}): 3330, 3303, 3222, 3161, 1516, 1490, 1435, 1301, 1280, 1158, 1110, 1071, 1014, 954, 786, 731. Anal. calcd for (%) for $\text{C}_4\text{H}_{10}\text{N}_{12}\text{O}_6$ (322.20): C 14.91, H 3.13, N 52.17; found C 14.78, H 3.02, N 52.32.

Diaminomethaniminium 5, 5'-dinitroamino-2, 2'-bi(1, 3, 4-oxadiazolate)(6)

Guanidine carbonate (1.0 mmol) was added to a solution of compound **2** (0.258 g, 1.0 mmol) in 30 mL of acetonitrile and the mixture was stirred at room temperature. After 2 h the precipitate was filtered, washed with ether and air-dried to yield. 0.312 g of compound **6** was obtained as a yellow solid in a yield of 82.9%. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 6.93 (s, 12H). ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ : 166.05 (s), 157.91 (s), 148.36 (s). IR (KBr, ν/cm^{-1}): 3386, 3270, 3205, 1681, 1657, 1525, 1494, 1407, 1297, 1155, 1074, 635. Anal. calcd for (%) for $\text{C}_6\text{H}_{12}\text{N}_{14}\text{O}_6$ (376.25): C 19.15, H 3.21, N 52.12; found: C 19.03, H 3.42, N 52.24.

Amino(hydrazinyl)methaniminium 5, 5'-dinitroamino-2, 2'-bi(1, 3, 4-oxadiazolate)(7)

Aminoguanidine bicarbonate (2.0 mmol) was added to a solution of compound **2** (0.258 g, 1.0 mmol) in 30 mL of acetonitrile and the mixture was stirred at room temperature. After 2 h the precipitate was filtered, washed with ether and air-dried to yield. 0.352 g of compound **7** was obtained as a yellow solid in a yield of 86.6%. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ : 8.56 (s, 2H) δ : 7.02 (s, 8H) δ : 5.36 (s, 4H). ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ : 164.65(s), 158.76(s), 146.85(s). IR (KBr, ν/cm^{-1}): 3385, 3310, 3164, 1664, 1590, 1522, 1488, 1403, 1277, 1153, 1073, 1016, 956, 776, 660. Anal. calcd for (%) for $\text{C}_6\text{H}_{14}\text{N}_{16}\text{O}_6$ (406.28): C 17.74, H 3.47, N 55.16; found: C 17.68, H 3.52, N 55.22.

Di(1, 2, 4-triazolium) 5, 5'-dinitroamino-2, 2'-bi(1, 3, 4-oxadiazolate)(8)

1, 2, 4- Triazole (2.0 mmol) was added to a solution of compound **2** (0.258 g, 1.0 mmol) in 30 mL of acetonitrile and the mixture was stirred at room temperature. After 2 h the precipitate was filtered, washed with ether and air-dried to yield. 0.347 g of

compound **8** was obtained as a white solid in a yield of 87.6%. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ : 10.06 (br.), 8.97(s, 4H). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ : 164.33(s), 146.48(s), 144.53(s). IR(KBr, ν/cm^{-1}): 3105, 1568, 1526, 1491, 1451, 1322, 1295, 1264, 1159, 1077, 1018, 945, 735, 625. Anal. calcd for(%) for $\text{C}_8\text{H}_8\text{N}_{14}\text{O}_6$ (396.24): C 24.25, H 2.04, N 49.49; found: C 24.20, H 2.11, N 49.53.

Di (3-amino-1, 2, 4-triazolium) 5, 5'-dinitroamino-2,2'-bi(1,3,4-oxadiazolate) (9)

3-Amino-1,2,4-triazole (2.0 mmol) was added to a solution of compound **2** (0.258 g, 1.0 mmol) in 30 mL of acetonitrile and the mixture was stirred at room temperature. After 2 h the precipitate was filtered, washed with ether and air-dried to yield. 0.362 g of compound **9** was obtained as a white solid in a yield of 84.9%. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ : 8.27 (s, 2H) δ : 8.05 (br.). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ : 165.94 (s), 151.11 (s), 148.11 (s), 139.64 (s). IR (KBr, ν/cm^{-1}): 3405, 3149, 2738, 1691, 1572, 1548, 1503, 1456, 1323, 1281, 1161, 1135, 1084, 1024, 946, 914, 887, 774,728. Anal. calcd for (%) for $\text{C}_8\text{H}_{10}\text{N}_{16}\text{O}_6$ (426.27): C 22.54, H 2.36, N 52.57; found: C 22.21, H 2.39, N 52.49.

Di (4-amino-1, 2, 4-triazolium) 5, 5'-dinitroamino-2,2'-bi(1,3,4-oxadiazolate) (10)

4-Amino-1,2,4-triazole (2.0 mmol) was added to a solution of compound **2** (0.258 g, 1.0 mmol) in 30 mL of acetonitrile and the mixture was stirred at room temperature. After 2 h the precipitate was filtered, washed with ether and air-dried to yield. 0.356 g of compound **10** was obtained as a white solid in a yield of 83.5%. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ : 9.25 (s, 4H), 8.43 (br). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ : 164.86 (s), 147.03 (s), 144.07 (s). IR (KBr, ν/cm^{-1}): 3312, 3120, 1571, 1555, 1537, 1493, 1495, 1322, 1277, 1161, 1086, 1040, 1019, 984, 798, 784, 622. Anal. calcd for (%) for $\text{C}_8\text{H}_{10}\text{N}_{16}\text{O}_6$ (426.27): C 22.54, H 2.36, N 52.57; found: C 22.37, H 2.48, N 52.31.

Didiaminouronium 5,5'-dinitroamino-2,2'-bi(1,3,4-oxadiazolate) (11)

Carbohydrazide (2.0 mmol) was added to a solution of compound **2** (0.258 g, 1.0 mmol) in 30 mL of acetonitrile and the mixture was stirred at room temperature. After 2 h the precipitate was filtered, washed with ether and air-dried to yield. 0.392 g of compound **11** was obtained as a white solid in a yield of 89.5%. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ : 8.50. ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ : 166.11 (s), 159.14 (s), 148.38 (s), IR (KBr, ν/cm^{-1}): 3320, 3275, 3213, 1697, 1623, 1602, 1555, 1529, 1492, 1429, 1350, 1316, 1281, 1220, 1168, 1120, 1083, 1019, 843, 776, 690. Anal. calcd for (%) for $\text{C}_6\text{H}_{14}\text{N}_{16}\text{O}_8$ (438.28): C 16.44, H 3.22, N 51.13; found: C 16.40, H 3.54, N 50.28.

3 Results and Discussion

3.1 Single Crystal Structure Analysis

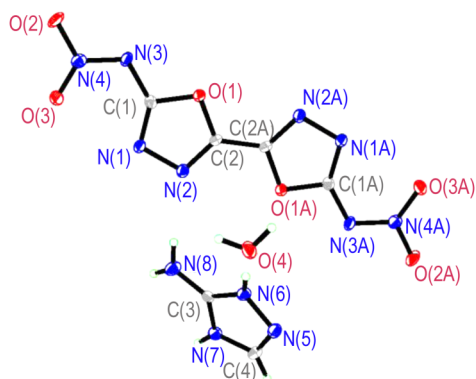
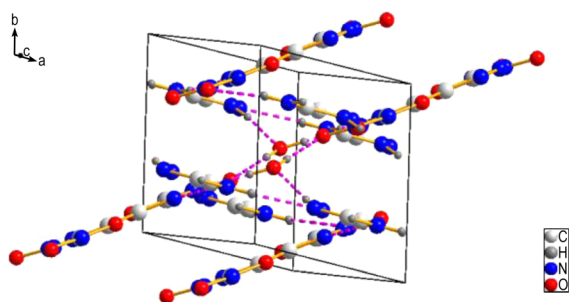
A solvent evaporation method was applied to grow good quality crystals of $\mathbf{9}\cdot 2\text{H}_2\text{O}$ and compound **10** for X-ray diffraction. The crystals of $\mathbf{9}\cdot 2\text{H}_2\text{O}$ and compound **10** were grown from a solution of water/ CH_3OH . Their structures are shown in Fig.1 to 4 and the crystallographic and structural refinement data are listed in Table 1.

Compound $\mathbf{9}\cdot 2\text{H}_2\text{O}$ crystallizes in the triclinic space group $P\bar{1}$ with one formula unit in the unit cell and a calculated density of $1.761\text{ g}\cdot\text{cm}^{-3}$ at 172(2) K. The asymmetric unit consists of one 3-amino-1,2,4-triazole cation, one and a half 5,5'-dinitroamino-2,2'-bi(1,3,4-oxadiazolate) anion and a lattice water molecule. As shown in Fig.1, the anion exhibits a central symmetric structure where an inversion centre lies. The packing diagram of $\mathbf{9}\cdot 2\text{H}_2\text{O}$ is built up by hydrogen bonds(Fig.2). The cations connect to anions by the classical hydrogen bonds ($\text{N}(7)\text{—H}(7)\cdots\text{O}(2)$, $2.800(2)\text{ \AA}$; $\text{N}(7)\text{—H}(7)\cdots\text{N}(3)$, $3.051(2)\text{ \AA}$; $\text{N}(7)\text{—H}(7)\cdots\text{N}(4)$, $3.353(2)\text{ \AA}$; $\text{N}(8)\text{—H}(8)\cdots\text{N}(2)$, $3.021(2)\text{ \AA}$) and the extensive hydrogen-bonding in the structure may also contribute to its good thermal stability.

Compound **10** crystallizes in the monoclinic space group $P2_1/c$ with $Z=2$ and a cell volume of

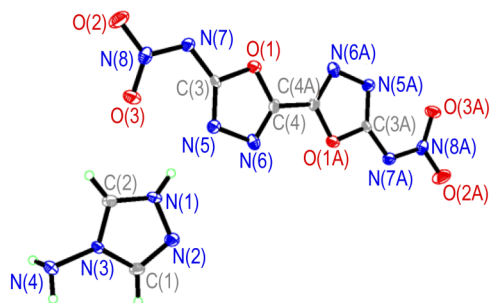
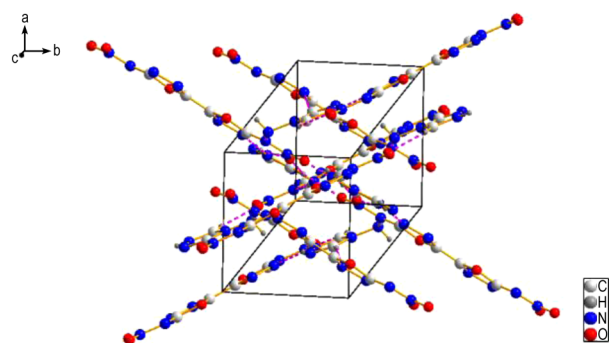
Table 1 Crystallographic data for **9**·2H₂O and **10**

crystal	9 ·2H ₂ O	10
CCDC	1544254	1543503
formula	C ₈ H ₁₀ N ₁₆ O ₆ ·2H ₂ O	C ₈ H ₁₀ N ₁₆ O ₆
formula mass	462.35	426.32
temperature /K	172(2)	171(2)
crystal system	triclinic	monoclinic
space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>
volume /Å ³	435.87(6)	812.65(14)
<i>a</i> /Å	6.0458(5)	6.9450(6)
<i>b</i> /Å	6.6277(6)	6.3230(6)
<i>c</i> /Å	11.3541(9)	18.576(2)
α /(°)	97.206(3)	90
β /(°)	101.955(3)	94.983(4)
γ /(°)	97.438(3)	90
<i>Z</i>	1	2
ρ /g·cm ⁻³	1.761	1.742
<i>F</i> (000)	238.0	436
<i>F</i> ²	1.050	1.031
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.0612, 0.0887	0.0851, 0.1087
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0413, 0.0816	0.0511, 0.0973

**Fig.1** Molecular structure of **9**·2H₂O**Fig.2** Ball and stick packing diagram of **9**·2H₂O

812.65(14) Å³. A density of 1.742 g·cm⁻³ was determined at 171 K from the X-ray diffraction analysis. As presented in Fig. 3, the structure of anion is similar to that of compound **10** and there are little differences in

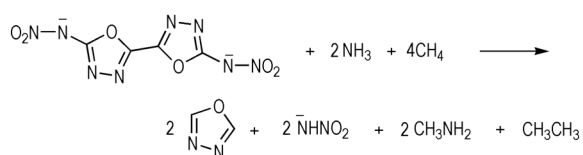
bond lengths and angles. The anion within the asymmetric unit (—CNNOC—N—NO₂) is nearly coplanar with an root mean square deviation value of 0.0237 Å. As can be seen from Fig. 4, large amount of hydrogen bonds can be found between the anions and cations (N(1)—H(1)···O(3), 2.888(3) Å; N(1)—H(1)···N(5), 2.726(3) Å; N(4)—H(4)···N(7), 2.984(4) Å). The oxygen atoms (O(2), O(3)) in the anions are involved in the formation of non-classical hydrogen bonds with the CH fragments (C(2)—H(2)···O(3), 2.950(3) Å; C(2)—H(2)···O(2), 3.024(4) Å).

**Fig.3** Molecular structure of compound **10****Fig.4** Ball and stick packing diagram of compound **10**

3.2 Computational Details

Computations were performed by using the Gaussian 09 suite of programs. The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP) functional with the 6-311+G** basis set^[21]. All the optimized structures were characterized to be local energy minima on the potential surface without imaginary frequencies. Atomization energies were calculated by the CBS-4M. The lattice energy of the trinitroethyl derivatives were predicted by the formula suggested by Jenkins et al.

The predictions of heats of formation (HOF) used the hybrid DFT/B3LYP methods with the 6-311+G** basis set through designed isodesmic reactions. The isodesmic reaction processes, that is, the number of each kind of formal bond is conserved, were used with the application of the bond separation reaction (BSR) rules. The molecule was broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reactions used to derive the HOF of compounds **3–11** are shown in Scheme 2.



Scheme 2 Isodesmic reactions of N,N' -([2,2'-bi(1,3,4-oxadiazole)]-5,5'-diyl)dinitramide anion

The change of enthalpy for the reactions at 298K can be expressed by Equ.(1):

$$\Delta H_{298\text{K}} = \sum \Delta_f H_p - \sum \Delta_f H_R \quad (1)$$

Where $\sum \Delta_f H_p$ and $\sum \Delta_f H_R$ are the HOF of the reactants and products at 298 K, respectively, and $\Delta H_{298\text{K}}$ can be calculated from the following expression in Equ.(2):

$$\Delta H_{298\text{K}} = \Delta E_{298\text{K}} + \Delta(pV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \quad (2)$$

where ΔE_0 is the change in total energy between the products and the reactants at 0 K; ΔZPE is the difference between the zero-point energies (ZPE) of the products and the reactants at 0 K. ΔH_T is the thermal correction from 0 to 298 K. The $\Delta(pV)$ value in Equ.(2) is the pV work term. It equals ΔnRT for the reactions of an ideal gas. For the isodesmic reactions $\Delta n=0$, so $\Delta(pV)=0$. On the left side of Equ.(2) apart from target compound all the others are called reference compounds. The HOF of reference compounds are available either from experiments or from the high level computing such as CBS-4M.

Based on a Born-Haber energy cycle (Scheme 3), the heat of formation of a salt can be simplified by Equ.(3):

$$\Delta H_f^0(\text{ionic salt}, 298\text{K}) = \Delta H_f^0(\text{cation}, 298\text{K}) + \Delta H_f^0(\text{anion}, 298\text{K}) - \Delta H_L \quad (3)$$

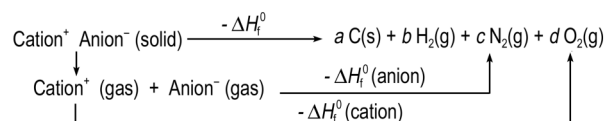
where ΔH_L is the lattice energy of the salt which could be predicted by the formula suggested by Jenkins et al^[22], as given in Equ.(4):

$$\Delta H_L = U_{\text{POT}} + [p(n_M/2-2) + q(n_X/2-2)]RT \quad (4)$$

where n_M and n_X depend on the nature of the ions Mp^+ and Xq^- , respectively, and are Equ.(3) for monatomic ions, Equ.(5) for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} takes the form of Equ.(5):

$$U_{\text{POT}} = \gamma(\rho_m/M_m)^{1/3+\delta} \quad (5)$$

where ρ_m is the density, $\text{g}\cdot\text{cm}^{-3}$. M_m is the chemical formula mass of the ionic material and the coefficients γ , $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{cm}^{\delta}$ are 8375.6 and $-178.8\text{kJ}\cdot\text{mol}^{-1}$, respectively.



Scheme 3 Born-Haber cycle for the formation of energetic salts

3.3 Physicochemical Properties

Thermal stability is one of the most important physicochemical properties of energetic materials. The thermal stabilities of compounds **3–11** were determined by differential scanning calorimetry (DSC) at a heating rate of $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ using dry nitrogen in Al pans. For all compounds, the decomposition temperatures were determined by the decomposition onset temperatures. As show in Fig. 5, all the compounds decompose directly without melting, and except for compound **3**, that melts at $73.5\text{ }^\circ\text{C}$. In particular, the decomposition process of **4–6**, and **9** possess two steps with the onset temperatures. The decomposition onset temperatures of the energetic compounds are observed in a range from $146.7\text{ }^\circ\text{C}$ (**4**) to $239.9\text{ }^\circ\text{C}$ (**6**). Compounds **6–10** are observed in a range from $181.7\text{ }^\circ\text{C}$ (**9**) to $239.9\text{ }^\circ\text{C}$ (**6**). As is known, thermal stability above $180\text{ }^\circ\text{C}$ is an essential requirement for energetic compounds for adaptation for practical use^[22]. The guanidinium salt **6** is the most thermally stable one at $239.9\text{ }^\circ\text{C}$. Both compound **6** and **9** have higher decomposition temperatures than

RDX (204°C).

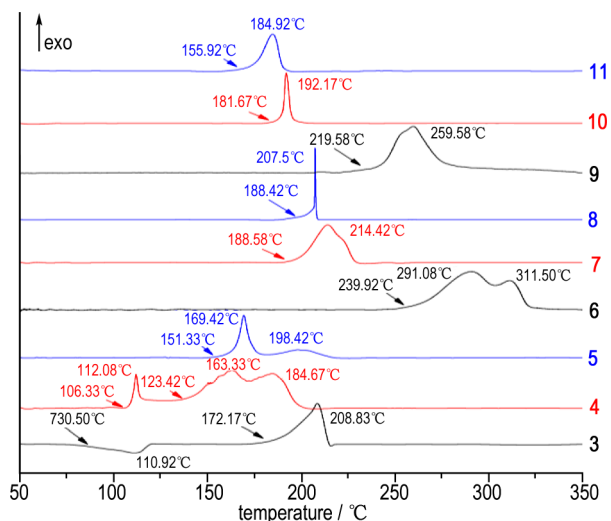


Fig.5 DSC curves of compounds 3–11

3.4 Energetic Performance

Impact and friction sensitivities are high priorities for secondary explosives. Low sensitivities of energetic materials can reduce the risk of serious and fatal accidents during the applications. Compounds 3–11 were tested for their sensitivity towards friction and impact using the BAM methods. The impact and friction sensitivities of compounds 3–11 fall in the range of 10–28 J or 120–280 N. The energetic salts are well stabilized and exhibit better impact and fric-

tion sensitivities (10–28 J for IS and 160–360 N for FS) than their parent compounds. All the compounds are less sensitive than RDX (7.5 J), the IS values of 3–4, 6–11 are higher than that of TNT (15 J). In the terms of the friction sensitivities, all of the energetic salts are much higher than RDX (120 N). By comparing with nitrogen-rich cations, the salts have additional ionic and hydrogen bonding, and thus exhibit lower impact and friction sensitivities.

The enthalpy of formation (HOF) is essential for calculating the detonation performance. The heats of formation of the synthesized compounds 3–11 were calculated based on appropriate isodesmic reactions. Calculations were carried out using the Gaussian 09 program suite. The geometry optimization of the structures and frequency analyses were carried out using the B3LYP functional with the 6-311+G** basis set. All of the optimized structures were characterized by true local energy minima on the potential energy surface without imaginary frequencies. The results are summarized in Table 2, the enthalpy of formation ranging from $-0.671(6)$ $\text{kJ}\cdot\text{g}^{-1}$ to 1.143 $\text{kJ}\cdot\text{g}^{-1}$ (10). With the exception of 3, 4 and 6, the energetic salts possess positive heats of formation, which are higher than TNT (-1.30 $\text{kJ}\cdot\text{g}^{-1}$) and RDX (0.32 $\text{kJ}\cdot\text{g}^{-1}$) due to a large number of C—N and N—N bonds, and

Table 2 The physicochemical properties of 3–11 compared with trinitrotoluene (TNT), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine(HMX)

compounds	$T_m / ^\circ\text{C}$	$T_d / ^\circ\text{C}$	OB / %	$\rho / \text{g}\cdot\text{cm}^{-3}$	$\Delta H_f / \text{kJ}\cdot\text{mol}^{-1}$	$D / \text{m}\cdot\text{s}^{-1}$	p / GPa	IS / J	FS / N
3	73.5	172.2	-32.85	1.941	-125.1	9136	34.2	20	180
4	—	146.8	-19.74	1.926	-121.55	9078	33.9	16	160
5	—	151.3	-34.76	1.937	113.40	9012	34.1	10	160
6	—	239.9	-51.03	1.711	-252.57	7693	21.3	28	280
7	—	188.6	-55.13	1.692	155.16	8100	24.1	24	240
8	—	188.4	-56.53	1.727	382.29	7886	23.9	26	280
9	—	219.6	-56.31	1.751	303.40	7984	24.0	25	360
10	—	181.7	-56.31	1.739	602.68	8181	25.8	22	360
11	—	155.9	-40.15	1.683	106.21	8147	25.2	26	360
TNT ^[4]	80.4	295	-73.8	1.654	-295	6881	19.5	15	—
RDX ^[23]	—	204	-21.6	1.80	70.3	8795	34.9	7.5	120
HMX ^[18]	—	280	-21.6	1.91	106.63	9320	39.5	7.4	120

Note: T_m is melting point. T_d is decomposition temperature from DSC ($5^\circ\text{C}\cdot\text{min}^{-1}$). OB is oxygen balance (%) for $\text{C}_a\text{H}_b\text{N}_c\text{O}_d$, and $\text{OB}\% = 1600 \times (d - 2a - b/2) / \text{Mw}$ (based on carbon dioxide). ρ is density measured using a gas pycnometer (25°C). ΔH_f is calculated molar enthalpy of formation. D is calculated detonation velocity. p is calculated detonation pressure. IS is impact sensitivity. FS is friction sensitivity

compound **10** has the highest value of $1.143 \text{ kJ}\cdot\text{g}^{-1}$.

By using the calculated heats of formation and the experimental densities (gas pycnometer) of the new energetic compounds, the detonation pressures (p) and detonation velocities (D) were calculated by using the EXPLO5 v6.02 program. As is shown in Table 2, the calculated detonation velocities fall in the range between $7693 \text{ m}\cdot\text{s}^{-1}$ (**6**) and $9136 \text{ m}\cdot\text{s}^{-1}$ (**3**), and detonation pressures range from 21.3 GPa(**6**) to 34.2 GPa(**3**). Compound **3–5** show excellent detonation properties which are much higher than those of RDX ($8795 \text{ m}\cdot\text{s}^{-1}$, 34.9 GPa), and to those of HMX ($9320 \text{ m}\cdot\text{s}^{-1}$, 39.6 GPa).

4 Conclusions

A new family of energetic salts featuring bi(1, 3, 4-oxadiazole) were prepared and fully characterized. In addition, the structures of **9**·2H₂O and **10** were confirmed by single-crystal X-ray diffraction analysis. According to the DSC results, most of the energetic salts showed acceptable thermal stabilities, with the decomposition temperatures ranging from 146.8 to 239.9 °C. The calculated detonation velocities lie in the range between 7693 (**6**) and 9136(**3**) $\text{m}\cdot\text{s}^{-1}$, and the detonation pressures range from 21.3 to 34.2 GPa, which are larger than those of TNT. The detonation velocities and pressures of compounds **3–5** are comparable to those of RDX. Based on the impact and friction tests, all the salts are less sensitive than RDX. Ammonium salt which has excellent detonation properties ($D=9136 \text{ m}\cdot\text{s}^{-1}$, $p=34.2 \text{ GPa}$) and acceptable sensitivities ($IS=20 \text{ J}$, $FS=180 \text{ N}$) is a promising potential candidate for energetic materials.

Reference:

- [1] ZHANG Qing-hua, HE Chun-lin, YIN Ping, et al. Insensitive nitrogen-rich materials incorporating the nitroguanidyl functionality [J]. *Chemistry-an Asian Journal*, 2014, 9 (1) : 212–217.
- [2] GAO Hai-xiang, Shreeve J M. Azole-based energetic salts[J]. *Chemical Reviews*, 2011, 111(11): 7377–7436.
- [3] WANG Rui-hu, XU Hong-yan, GUO Yong, et al. Bis[3-(5-nitroimino-1, 2, 4-triazolate)]-based energetic salts: synthesis and promising properties of a new family of high-density insensitive materials[J]. *Journal of the American Chemical Society*, 2010, 132(34): 11904–11905.
- [4] WANG Kai, Parrish D A, Shreeve J M. 3-Azido-*N*-nitro-1*H*-1, 2, 4-triazol-5-amine-based energetic salts [J]. *Chemistry-A European Journal*, 2011, 17(51): 14485–14492
- [5] ZHANG Jia-heng, Dharavath S, Mitchell L A, et al. Energetic salts based on 3,5-bis(dinitromethyl)-1,2,4-triazole monoanion and dianion: controllable preparation, characterization, and high performance [J]. *Journal of the American Chemical Society*, 2016, 138(24): 7500–7503
- [6] Klapötke T M, Mayr N, Stierstorfer J, et al. Maximum compaction of ionic organic explosives: bis(hydroxylammonium) 5, 5'-dinitromethyl-3, 3'-bis(1, 2, 4-oxadiazolate) and its derivatives[J]. *Chemistry-A European Journal*, 2014, 20(5): 1410–1417.
- [7] DENG Mu-chong, ZHANG Qing-hua, WANG Kang-cai, et al. Synthesis and properties of 5, 10-bis(dinitromethyl)-furan [3,4-e]bis([1,2,4]triazolo)[4,3-a:3',4'-c] pyrazine and its energetic ion compounds[J]. *Chinese Journal of Energetic Materials(Hanneng Cailiao)*, 2018, 26(2):144–149.
- [8] LI Ya-nan, SHU Yuan-jie, ZHANG Sheng-yong, et al. Synthesis and thermal Properties of 4, 4', 5, 5'-Tetranitro-2, 2'-bimidazole and its energetic ion salts[J]. *Chinese Journal of Energetic Materials(Hanneng Cailiao)*, 2017, 25(4): 298–303.
- [9] WANG Rui-hu, GUO Yong, ZENG Zhuo, et al. Furazan-functionalized tetrazolate-based salts: a new family of insensitive energetic materials [J]. *Chemistry-A European Journal*, 2009, 15(11): 2625–2634.
- [10] WANG Rui-hu, GUO Yong, SA Rong-jian, et al. Nitroguanidine-fused bicyclic guanidinium salts: a family of high-density energetic materials[J]. *Chemistry-A European Journal*, 2010, 16(28): 8522–8529
- [11] TANG Yong-xing, ZHANG Jia-heng, Mitchell L A, et al. Taming of 3, 4-di(nitramino) furazan [J]. *Journal of the American Chemical Society*, 2015, 137(51):15984–15987
- [12] TANG Yong-xing, GAO Hai-xiang, Mitchell L A, et al. Syntheses and promising properties of dense energetic 5, 5'-dinitramino-3, 3'-azo-1, 2, 4-oxadiazole and its salts [J]. *Angewandte Chemie International Edition*, 2016, 55 (9) : 3200–3203.
- [13] HAO Wei, HE Chun-lin, ZHANG Jia-heng, et al. Combination of 1, 2, 4-oxadiazole and 1, 2, 5-oxadiazole moieties for the generation of high-performance energetic materials[J]. *Angewandte Chemie International Edition*, 2015, 54 (32) : 9367–9371.
- [14] HE Chun-lin, TANG Yong-xing, Mitchell L A, et al. N-oxides light up energetic performances: synthesis and characterization of dinitraminobisfuroxans and their salts[J]. *Journal of Materials Chemistry A*, 2016, 4(23): 8969–8973.
- [15] WANG Zuo-quan, ZHANG Hong, Killian B J, et al. Synthesis, characterization and energetic properties of 1, 3, 4-oxadiazoles[J]. *European Journal of Organic Chemistry*, 2015, 2015 (23): 5183–5188.
- [16] WU Qiong, ZHU Wei-hua, XIAO He-ming. Molecular design of trinitromethyl-substituted nitrogen-rich heterocycle derivatives with good oxygen balance as high-energy density compounds[J]. *Structural Chemistry*, 2013, 24(5):1725–1736.
- [17] TIAN Jia-wei, XIONG Hua-lin, LIN Qiu-han, et al. Energetic

- compounds featuring bi(1,3,4-oxadiazole): a new family of insensitive energetic materials [J]. *New Journal of Chemistry*, 2017, 41(5): 1918–1924.
- [18] YU Qiong, YIN Ping, ZHANG Jia-heng, et al. Pushing the limits of oxygen balance in 1,3,4-oxadiazoles [J]. *Journal of the American Chemical Society*, 2017, 139(26): 8816–8819.
- [19] Hermann T S, Karaghiosoff K, Klapötke T M, et al. Synthesis and characterization of 2,2'-dinitramino-5,5'-bi(1-oxa-3,4-diazole) and derivatives as economic and highly dense energetic materials [J]. *Chemistry-A European Journal*, 2017, 23(50): 12092–12095.
- [20] ZHANG Wen-quan, ZHANG Jia-heng, DENG Mu-chong, et al. A promising high-energy-density material [J]. *Nature Communication*, 2017, 8(1): 181–187.
- [21] Hariharan P C, Pople J A. Influence of polarization functions on MO hydrogenation energies [J]. *Theoretica Chimica Acta*, 1973, 23(8): 213–216.
- [22] Jenkins H D B, Tudeal D, Glasser L. Lattice potential energy estimation for complex ionic salts from density measurements [J]. *Inorganic Chemistry*, 2002, 41(9): 2364–2367.
- [23] Klapötke T M, Penger A, Pflüger C, et al. Advanced open-chain nitramines as energetic materials: heterocyclic-substituted 1,3-dichloro-2-nitrazapropane [J]. *European Journal of Inorganic Chemistry*, 2013, 2013(26): 4667–4678.

5,5'-二硝胺基-2,2'-联-1,3,4-噁二唑含能离子盐的合成及性能

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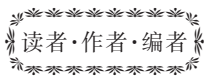
摘要: 以5,5'-二硝胺基-2,2'-联-1,3,4-噁二唑为原料合成了一系列含能盐,采用了红外(FT-IR)、核磁(NMR)和元素分析进行了结构表征。并用X-射线单晶衍射进一步确定了3-氨基-1,2,4-三唑盐(**9**·2H₂O)和4-氨基-1,2,4-三唑盐(**10**)的结构,用差热扫描法(DSC)测定了它们的热分解温度,用Explos 5 v6.02计算了它们的爆轰性能。结果表明它们的热分解温度范围为146.8~239.9℃;计算爆速高于7693 m·s⁻¹,爆压高于21.3 GPa;密度介于1.683~1.941 g·cm⁻³,实测撞击感度介于10~28 J,摩擦感度介于160~360 N,表明5,5'-二硝胺基-2,2'-联-1,3,4-噁二唑类含能盐是一类性能较好的高能量密度材料。

关键词: 含能材料;1,3,4-噁二唑;X-射线单晶衍射;感度;爆轰性能

中图分类号: TJ55; O62

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《含能材料》“含能共晶”征稿

含能共晶是不同含能分子通过氢键等相互作用力形成的具有稳定结构和性能分子晶体。含能共晶充分组合了单质含能分子的优点,呈现出感度低,综合性能优良的特点,具有潜在的应用前景,共晶研究已经引起国内外含能材料学界的高度关注。为推动含能共晶的研究和交流,本刊特推出“含能共晶”专栏,主要征稿范围包括含能共晶晶体设计与性能预测、含能共晶的制备、结构解析、性能等。来稿请注明“含能共晶”专栏。