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Incorporating Energetic Moieties into a Four Oxadiazole Rings System for the Generation of High-Performance Energetic Materials

Bohan Wang^[a] Hualin Xiong^[a] Guangbin Cheng^[a] and Hongwei Yang^{*[a]}

Abstract: The synthesis of three neutral 3,3'-di(1,2,5-oxadiazol-3yl)-5,5'-bi(1,2,4-oxadiazole) in combination with different energetic nitrimino, trinitroethylamino and moieties like N-nitrated trinitroethylamino is presented. In addition, a novel family of energetic salts based on 4,4'-([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diyl)bis(1,2,5-oxadiazol-3-nitramide) were synthesized. The new compounds (4, 6-18) were characterized by IR, multinuclear NMR spectroscopy and elemental analysis. The structures of 4.2C4H8O2, 9, 13, 15 and 16 were further confirmed by single crystal X-ray diffraction. The thermal stabilities of 4, 6-18 were determined by differential scanning calorimetry (DSC). Most of the new compounds have high densities (1.72-1.93 g cm⁻³) measured using a gas pycnometer (25 °C), In addition, energetic evaluation indicates that they also have good detonation pressures and velocities (P: 26.4-41.9 GPa; D: 8218-9550 m s⁻¹).

Introduction

The synthesis towards new energetic materials with excellent performance characteristics is an ongoing project in many research groups worldwide.¹ Due to practical application demands, the new materials have to meet many different standards such as high detonation performance, low sensitivity, environmental compatibility, safety concerns.^{2,3} However, materials with high stability and low sensitivity often exhibit a poor energetic performance.⁴ Considerable effort has been attempted to coordinate the inherent contradiction between the performance and sensitivity of energetic molecules. An effective approach is the combination of a few of the same or different heterocyclic subunits in a molecule.⁵

Compounds containing heterocyclic ring systems are of great importance both medicinally and industrially.⁶ For example, oxadiazoles in different regioisomeric forms (Figure 1), are of considerable interest in different areas of medicinal and pesticide chemistry and also polymer and material science.⁷ In particular, the energetic materials based on azole frameworks are highly desirable, such as tetrazoles, 1,2,5-oxadiazoles (furazans) and 1,2,5-oxadiazole-2-oxides (furoxans),⁸ which

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Figure. 1 Oxadiazole rings can exist in different regioisomeric forms. One 1,3,4-isomer and one 1,2,5-isomer and two 1,2,4-isomers (if asymmetrically substituted).





Figure. 2 Energetic compounds with nitroamino fragments.



Figure. 3 Energetic compounds with trinitroethylamino, N-nitrated trinitroethylamino and nitramino furazan fragments.

have high nitrogen content and high positive enthalpy. Among the combinations between functional moiety and azole backbone, the family of nitramino-furazans has gained considerable attention due to its high detonation performance.⁹ For example, 3,4-di(nitramino)furazan (**i**)¹⁰ (Fig.2) shows good detonation properties with a detonation pressure of 40.5 GPa and a detonation velocity of 9376 m s⁻¹. However, it has a poor decomposition temperature (99 °C), a high impact sensitivity (<5J) and a friction sensitivity (<5N). Another example is [2,2'bi(1,3,4-oxadiazole)]-5,5'-dinitramide (ICM-101), which exhibits a surprisingly high density (1.99 g cm⁻³ at 298K) and good detonation performances (P = 41.9 GPa; D = 9481 m s⁻¹).¹¹

Many studies have showed that the combination of two or more nitrogen-rich heterocycles can lead to excellent energetic properties.¹² To gain good detonation performance while minimizing sensitivity, 1,2,4-oxadiazole and 1,2,5-oxadiazole were incorporated with nitroamino-furazan.^{13,14} For example, the hydroxyammonium salt (ii) and hydrazinium (iii) (Fig.2) show not only good detonation performances (ii: P = 37.4 GPa; D =

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9046 m s⁻¹; iii : P = 30.1 GPa; D = 8603 m s⁻¹) but also acceptable sensitivities (ii : IS = 16 J; FS = 160 N; iii : IS = 19 J; FS = 240 N) with good thermal stabilities (ii : $T_d = 193$ °C; iii : $T_d = 234$ °C). Another example is compound iv (Figure. 3), which exhibits a detonation pressure of 46.1 GPa, velocity of 10114 m s⁻¹, a density of 2.12 g cm⁻³ and a thermal stability of 317 °C. In addition, introducing trinitroethylamino group into the furazan ring can increase the oxygen balance and lead to an excellent energetic performance.¹⁵ Recently, the trinitroethyl energetic derivatives based on aminofurazans have been reported and demonstrated outstanding performance^{15e} (v : P = 35.4 GPa, D = 8900 m s⁻¹; vi: P = 40.8 GPa, D = 9486 m s⁻¹) (Figure. 3).

As is seen for these furazan-based compounds, combination of furazan with 1,2,4-oxadiazole could be favorable for obtaining a high level of detonation performance while meeting the requirement of insensitivity. In addition, it has been reported that the more ring structures present in a molecule, the higher the heat of formation of the molecule will gain (in kJ mol⁻¹/kJ g⁻¹).¹⁶ It can be attributed to the presence of abundant nitrogen atoms and -C=N- bonds in the two rings system.^{16f} Herein, we reported and characterization 4,4'-([5,5'-bi(1,2,4-oxadiazole]]-3,3'-diyl)-bis(1,2,5-oxadiazol-3-nitramide) (4), which comprises two furazan and two 1,2,4-oxadiazole rings. In addition, some energetic salts (6-16) based on 4 were synthesised and fully characterized. To seek higher detonation performances of energetic materials, trinitroethyl fragments were successfully introduced into the framework of aminofurazan in this paper.

Syntheses

First, the intermediate product 4,4'-([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diyl)-bis(1,2,5-oxadiazol-3-amine) (3) was prepared by twostep reactions from malononitrile (1) according to literature methods.¹⁷ The synthetic pathway towards the nitramino product 4 and its energetic salts are illustrated in Scheme 1. Compound 4 was obtained by direct nitration of 3 using 100% nitric acid at 0 °C. The reaction mixture was guenched with ice and with stirring, then the precipitate was collected by filtration and washed with ice water. The energetic salts based on 4 were synthesized in acetonitrile by mixing 4 with a series of bases of ammonium (6), hydrazinium (7), hydroxylammonium (8), didiaminouronium (9), guanidinium (10), aminoguanidinium (11), 1,2,4-triazolium (14), 4-amino-1,2,4-triazolium (15) and 3amino-1,2,4-triazolium (16). Salts 12 and 13 were synthesized by using the silver salt 5 with the corresponding chloride salts. The impetus of these reactions was the formation of silver chloride, which had a very low solubility in water and could be easily removed by filtration. These energetic salts 6-16 were isolated in high yields (81.65-93.43%) and were stable in air. The trinitroethanol was synthesized according to the method reported previously.¹⁸ The N-trinitroethyl derivative 17 were synthesized via the reactions of the electron-deficient trinitroethanol with corresponding diamine compound 3 with a

yield of 89%. Then compound 17 was treated with 100% nitric

acid and acetic anhydride to afford the

trinitroethylamino product 18 with a yield of 83%.

Results and discussion



Scheme 1 Synthesis of energetic compounds base on 4,4'-([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diyl)-bis(1,2,5-oxadiazol-3-amine)

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Spectroscopy

The structures of the compounds 4, 6-18 were fully characterized by IR, NMR and elemental analysis. The ¹H NMR and ¹³C NMR spectra of these new compounds are shown in the Supporting Information.

In the ¹H NMR spectrum of compound **4**, the proton signal of an imino group attached to the furazan ring was observed at 7.70 ppm. In the ¹H NMR spectrum of **17**, the proton signals of -NHgroups attached to the furazan ring was observed at 6.82. The proton signals of the methylene group in the ¹H NMR spectrum of 17 were observed at 5.62 ppm. However, -CH2- protons shows lower field of 6.66 ppm in the ¹H NMR spectrum of **18** because of the electron withdrawing nature of the nitro group. In the ¹³C NMR spectrum of 4 and 6-18, four signals for two furazan and two 1,2,4-oxadiazole rings carbon atoms were found in the expected range as consequence of their symmetric structure. The carbon resonance of methylene in compound 17 and 18 were found at 47.82 and 53.02 ppm, and the carbon resonance of trinitromethyl in them were found at 125.55 and 122.81 ppm, respectively, which are in good agreement with previously recorded shifts for similar compounds.^{18a}

X-ray crystallography

Compound 4, salts 9, 13, 15 and 16 were confirmed by singlecrystal X-ray diffraction. Compound 4 were obtained by the slow solvent evaporation of 1,4-dioxane solution while salts 9, 13, 15 and 16 were obtained by the slow solvent evaporation of the water and methanol solution at room temperature. Their crystal and structure data are listed in Table 1 and their structures are shown in Figure. 4a-8a. Selected bond lengths, angles, torsion angles and hydrogen bonds are listed in the Supporting Information (Table S2-S16).

Compound 4 crystallizes in the triclinic P1 space group, with one molecule in the unit cell and with a calculated density (1.505 g cm⁻³) as a dioxane solvate. The non-solvated density of 4 (1.897 g cm⁻³) was calculated by using powder diffraction, more data can be found in Supporting Information (Table S17). Its molecular structure is shown in Figure. 4a. The bond lengths of N1-O1 (1.404(3) Å), C1-N1 (1.303(3) Å), N2-C1 (1.384(3) Å), C2-O1 (1.383(3) Å) are normal in the 1,2,4-oxadiazole ring.¹⁹ The two 1,2,4-oxadiazole rings show a planar arrangement, which is reflected in the torsion angles C1-N2-C2-C2A 176.3(2)°, N2-C2-C2A-O1A -0.7(4)° and the furazan rings are twisted out of the plane as indicated by the dihedral angle of 12°. The nitro group is twisted out of the furazan rings plane by 105° $(N6-N5-C3-N3\ 109.5(3)^{\circ},\ N6-N5-C3-C4\ -78.7(4)^{\circ})$. As can be seen from Figure. 3c, the 3,3'-di(1,2,5-oxadiazol-3-yl)-5,5'bi(1,2,4-oxadiazole) planes form a face-to-face stacking in which the solvated 1,4-dioxane molecules are parallel to one another. It has been reported that the highly ordered structures formed in layer-by-layer arrangements usually show fascinating material characteristics.²⁰ For example, TATB has low sensitivities (IS = 50 J; FS > 360 N), calculations indicate that the layer-stacking structure of this material can absorb the mechanical stimuliinduced kinetic energy by converting it to layer sliding, which results in low sensitivity.20 Fortunately, the structure of compound 4 is very similar to that of TATB with successive infinite 2D layers and highly ordered face-to-face 3D stacking (Fig.4c), which lead to its comparatively low sensitivities (IS = 16 J; FS > 240 N).

The molecular structure of 9, which crystallizes in the monoclinic space group $P2_1/c$, with a density of 1.809 g cm⁻³ at 173K, is shown in Figure. 5a. The N6-O3 and N6-O4 bonds of the nitro groups in salt 9 are elongated by 0.04 Å and 0.021 Å when compared with its neutral compound 4.2C4H8O2, respectively. The 1,2,4-oxadiazole rings and furazan rings in salt 9 are almost in the same plane with torsion angles (N1-C1-C4-C3 3.5(5)°, 01-C2-C2A-N2A N1-01-C2-C2A -179.2(2)°, -1.3(4)°). Interestingly, the exocyclic atom N5, N6, O3 and O4 (N5A, N6A,

O3A and O4A) are also almost in the same plane with the four rings (C3-N5-N6-O4 1.1(4)°, C3-N5-N6-O3 179.4(2)°, N6-N5-C3-C4 -172.5(2)°, N6-N5-C3-N3 8.8(4)°). The anions and cations are almost in the same plane, which can be seen from the 2D layer (Figure.5c), and a large amount of hydrogen bonds can be found between them (Figure.5b), these intramolecular hydrogen bonds combined with intermolecular hydrogen bonds to form a face-to-face stacking and make an important contribution to enhance the density of salt 9.







Figure. 5 (a) Single-crystal X-ray structure of 9; (b) Hydrogen bonds in 9; (c) Layer assembly and the face-to-face crystal packing for 9.

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TATB and 4.2C4H8O2.



Figure. 6 (a) Single-crystal X-ray structure of 13; (b) Hydrogen bonds in 13; (c) Layer assembly and the criss-crossed crystal packing for 13.



Figure. 7 (a) Single-crystal X-ray structure of 15; (b) Hydrogen bonds in 15; (c) Mixing crystal packing for 15.



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Figure. 8 (a) Single-crystal X-ray structure of 16; (b) Hydrogen bonds in 16; (c) Wave-like crystal packing for 16.

Salt **13** crystallizes in the monoclinic space group $P_{21/c}$, with two molecules per unit cell. The calculated density of 1.733 g cm³ was determined from its X-ray crystal structure at 173K (Figure.6a). The four heterocycles in the dianion are in nearly the same plane, the torsion angles N2-C2-C2A-N2A, C2-N2-C1-C4 and N2-C1-C4-C3 are 180.0(3)°, -178.1(2)° and 177.4(2)°, respectively. The nitramino groups are also nearly in the same plane as the furazan rings as indicated by the torsion angles (N6-N5-C3-C4 -178.7(2)°, C3-N5-N6-O3 2.9(3)°, C3-N5-N6-O4 - 178.4(2)°). The hydrogen-bonding (Figure.6b) interactions between the triaminoguanidine cations and the anions (N7-H7A···O3 2.53(3) Å, N7-H7A···N12 2.27(3) Å, N7-H7A···O4 2.50(3) Å, N8-H8A···N10 2.52(3) Å, N8-H8A···O4 2.58(3) Å and so on), playing an important role in forming the criss-crossed(Fig.6c) crystal packing of salt **13**.

Single-crystal X-ray diffraction revealed that salt **15** crystallizes in monoclinic *P*2₁/*c* space group, with a density of 1.796 g cm⁻³ at 173K (Figure. 7a). The length of the N-N bond in salt **15** (N5-N6 1.337(3) Å) is slight longer than that of salt **9** (N5-N6 1.323(3) Å). However, the average bond length of the N-O bonds in the nitro groups of salt **15** (1.248 Å) are slight shorter than that of salt **9** (1.252 Å). The bonds in the furazan rings and 1,2,4oxadiazole rings of salt 15 are nearly the same length as those in salts **9** and **13**. The cations and the anions are not in the same plane can be seen from Figure.7c. The hydrogen atom in the cation form intermolecular hydrogen-bond pairings with neighboring oxygen atoms in the nitramino group (N7-H7A···O4 2.39(3) Å, C6-H6···O3 2.4800 Å, C5-H5···O3 2.4400 Å) (Figure.6b). These hydrogen bonds make the packing structure of salt **15** show a mixing arrangement.

Salt 16 crystallizes in monoclinic P21/c space group with two molecules in the unit cell and the density is 1.761 g cm⁻³, which is shown in Fig. 8a. The deprotonation of compound 4 with 3amino-1,2,4-triazole to give salt 16 results in shorter N-NO2 (N5-N6 1.314(3) Å) and longer N-O bonds (N6-O3 1.272(3) Å, N6-O4 1.253(3) Å) than compound 4 (N5-N6 1.391(3) Å, N6-O3 1.222(3) Å, N6-O4 1.221(3) Å). The C2-C2A bond is 1.466(5) Å, the C1-C4 bond is 1.465(3) Å, the C-C bonded the two 1,2,4oxadiazole rings are essentially planar with a torsion angle (O1-C2-C2A-O1A -180.0(2)°), the C-C bonded furazan and 1,2,4oxadiazole rings shows a planar arrangement, which is reflected in the torsion angles (N2-C1-C4-C3 -176.9(3)°, N2-C1-C4-N4 2.8(4)°), while the nitramino group is twisted away from the furoxan ring with a torsion angle of 14.5°. In the packing diagram of 16, intermolecular hydrogen bonds (N8-H8A···O3 1.90(2) Å, N8-H8A…O4 2.55(3) Å, N8—H8A…N6 2.57(2) Å, N9-H9A…O4 2.08(3) Å, N9-H9A…N3 2.25(2) Å, N10-H10A…O4 2.09(3) Å, N10-H10B…O3 2.34(4) Å, N10-H10B…N5 2.24(4) Å, C6-H6…N4 2.50(4) Å) are observed (Fig. 8b). All the atoms in the cation are almost in the same plane, the anion planes are neatly inserted into the cation planes, as can be seen from Figure. 8c, making the packing structure of salt 16 show a wavelike arrangement.



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Table 1 Crystallographic data for 4·2C4H ₈ O ₂ , 9, 13,15 and 16								
Crystal	4.2C4H8O2	9	13	15	16			
Formula	C ₂₀ H ₂₆ N ₁₂ O ₁₄	C ₁₀ H ₁₄ N ₂₀ O ₁₀	C ₁₀ H ₁₈ N ₂₄ O ₈	$C_{12}H_{10}N_{20}O_8$	C ₁₂ H ₁₀ N ₂₀ O ₈			
Formula Weight	658.53	574.41	602.48	562.40	562.40			
Temperature (K)	173(2)	173(2))	173(2)	173(2)	173(2)			
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic			
Space group	<i>P</i> 1	<i>P</i> 2 ₁ /n	<i>P</i> 2 ₁ /c	P21/c	P21/c			
Volume [Å3]	726.54(13)	1054.4(2)	1154.81(17)	1039.9(2)	1060.4(2)			
a [Å]	6.6528(7)	10.2856(12)	6.6771(5)	8.0298(9)	11.9498(14)			
b [Å]	8.9943(9)	9.1849(11)	7.9630(7)	16.004(2)	6.8573(9)			
c [Å]	12.9685(14)	11.2424(10)	21.7734(19)	8.3865(11)	13.2689(18)			
α[°]	91.548(4)	90	90	90	90			
β[°]	102.237(4)	105.225(4)	94.039(3)	105.225(4)	102.775(5)			
γ[°]	105.854(3)	90	90	90	90			
Z	1	2	2	2	2			
ρ(calc) [g cm ⁻³]	1.505	1.809	1.733	1.796	1.761			
F2	1.023	1.051	1.053	1.023	1.055			
R ₁ ,wR ₂ [all data]	0.1022, 0.1205	0.1012, 0.1032	0.0793, 0.0942	0.0870, 0.0926	0.0999, 0.0961			
$R_{1}, wR_{2}[I \ge 2\sigma(I)]$	0.0558, 0.1038	0.0520, 0.0895	0.0450, 0.0834	0.0461, 0.0807	0.0485, 0.0824			
CCDC	1580359	1580367	1581858	1580365	1581859			

Energetic materials properties

The thermal stabilities of these new energetic compounds were examined using differential scanning calorimetric (DSC) measurements in the temperature range from 50 to 400 °C at heating rate of 5 °C min⁻¹ (Table 2). All the newly compounds (4, 6-18) are water insensitive and can be stored for long periods in air. The neutral compound 4 decomposes thermally at 100.8 °C, its salts (6-16) and the trinitroethylamino derivatives (17, 18) are more stable thermally with decomposition temperatures ranging from 151.8 (18) to 253.1 (10) °C. In particular, the decomposition process of 13 and 18 possess two steps with the temperature of 182.7 °C and 212.7 °C (13), 151.8 °C and 175.9 °C (18), respectively. The thermal stabilities of 7 (T_d =215.7 °C), 10 (T_d =253.1 °C) and 15 (T_d =219.1 °C) are higher than RDX ($T_d = 204 \text{ °C}$).

The density is an important parameter which plays an important role in calculation of energetic performance. Densities of compounds all new were measured by using a gas pycnometer at 25°C (Table2) and found to fall in the range of 1.72-1.93 g cm⁻³. Among them, 8 (1.82 g cm⁻³) and 17 (1.90 g cm⁻³) have relatively high densities that are comparable to that of RDX (1.80 g cm⁻³). More importantly, the densities of 4 (1.92 g cm⁻³) and **18** (1.93 g cm⁻³) are higher than HMX (1.91 g cm⁻³).

In order to study the detonation parameters of these new compounds, calculations were carried out using the Gaussian 09 program suite.²¹ The geometry optimization of the structures and frequency analyses were carried out using the B3LYPn

Table 2 The physicochemical properties of 4, 6-18 compared with 2,2'-bi(1,3,4-oxadiazole)]-5,5'-dinitramide(ICM-101), 2, 4, 6, 8, 10, 12-(hexanitrohexaaza)cyclododecane(CL-20), 2,4,6-triamino-1,3,5trinitrobenzene (TATB), 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine

(⊓IVI∧).				
Compounds	T _d ª [°C]	ρ ^ь [g m⁻¹]	<i>D</i> ^c [m s⁻¹]	P ^d [GPa]
4	100.8	1.92	9185	37.5
6	207.2	1.76	8489	30.5
7	215.7	1.76	8747	32.2
8	165.3	1.82	8863	35.0
9	209.2	1.80	8831	32.6
10	253.1	1.74	8218	26.4
11	211.8	1.74	8483	28.4
12	205.5	1.73	8515	28.1
13	182.7	1.72	8688	29.3
14	176.3	1.75	8287	28.1
15	219.1	1.78	8617	30.7
16	210.5	1.75	8343	28.2
17	187.7	1.90	9062	37.2
18	151.8	1.93	9550	41.9
ICM-101 ^e	210.0	1.99	9481	41.9
ε-CL-20 ^e	215	2.04	9455	46.7
TATB	360	1.93	8114	31.2
TNT	295	1.65	6881	19.5
RDX ^g	204	1.80	8795	34.9
HMX ^g	280	1.91	9144	39.2

^a Decomposition temperature from DSC (5 °C min⁻¹).^b Density measured using a gas pycnometer (25 °C). ^c Calculated detonation velocity. ^d Calculated detonation pressure. ^e Ref 9. ^f Ref 4(a). ^g Ref 4(c).

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functional with the 6-311+G** basis set.22 All the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

It was reported that heterocycles with higher nitrogen content show higher heats of formation.²³ All the new compounds exhibit positive heats of formation ranging between 741.61 (10) and 1573.01 (15) kJ mol⁻¹. By using calculated values of the heats of formation and experimental values for densities of the new compounds, the detonation pressures (P) and detonation velocities (D) of 4, 6-18 were calculated using the EXPLO5 v6.01 program.²⁴ The calculated detonation velocities and pressures are in the range from 8218 to 9550 m s⁻¹ and 26.4 to 41.9 GPa, respectively. Of these compounds, the energetic performances of 8 (D: 8863 m s⁻¹; P: 35.0 GPa) and 17 (D: 9062 m s⁻¹; P: 37.2 GPa) are comparable to RDX (D: 8795 m s⁻¹; P: 34.9 GPa). More strikingly, compound 4 is (D: 9185 m s⁻¹; P: 37.5 GPa) comparable to HMX (D: 9144 m s⁻¹; P: 39.2 GPa), compound **18** exhibits higher detonation properties, especially in terms of detonation velocity (9550 m s⁻¹) and pressure (41.9 GPa), which are similar to ICM-101 (*D*: 9481 m s⁻¹; *P*: 41.9 GPa) and CL-20 (D: 9455 m s⁻¹; P: 46.7 GPa).

Impact and friction sensitivities (IS and FS) of samples are measured and evaluated by using the standard BAM method,²⁵ as shown in Supporting Information (Table S18). Compound 4 has the relatively low impact sensitivity of 16 J and friction sensitivity of 240 N, which are comparable to TNT (IS: 15J; FS: 358N). Not surprisingly, compound 18 (IS: 4.5J; FS: 120N) have relatively high impact and friction sensitivities, which are similar to ICM-101 (IS: 5J; FS: 60N) and CL-20 (IS: 4J; FS: 48N). In addition, most of the energetic salts are very insensitive with IS > 40 J and FS > 360N.

Conclusions

In conclusion, We have successfully synthesized a new 4,4'-([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diyl)-bis(1,2,5compound. oxadiazol-3-nitramide), which has two furazan rings and two 1,2,4-oxadiazole rings linkages in one molecule was synthesized. Subsequently, a series of nitrogen-rich energetic salts (6-16) were synthesized and fully characterized. In addition, two trinitroethyl derivatives of compound 3 were synthesized by a simple way. All new compounds exhibited reasonable physical properties, such as a relatively high density (1.72-1.93 g cm⁻³) and good thermal stability (T_d = 151.8-253.1 °C, except for 4, 100.8 °C). More importantly, with a large number of N-O and N-N bonds in these new structures, the calculated heats of formation of 4, 6-18 are relatively high and fall in the range of 741.61 to 1573.01 kJ mol⁻¹ (1.425 to 2.797 kJ g⁻¹). Furthermore, most of the energetic salts have adequately acceptable sensitivities (IS > 40J, FS > 360N) and attractive detonation properties (D, 8218-8863 m s⁻¹; P, 26.4-35.0 GPa). In addition,

the detonation performances of compound **4** (*D*: 9185 m s⁻¹; *P*: 37.5 GPa) are comparable to HMX (*D*: 9144 m s⁻¹; *P*: 39.2 GPa), and its sensitivity properties (IS: 16J; FS: 240N) is similar to TNT (IS: 15J; FS: 358N). More importantly, the detonation performance and sensitivities of **18** (*D*: 9550 m s⁻¹, *P*: 41.9 GPa, IS: 4.5J; FS: 120N) are even similar to CL-20 (*D*: 9455 m s⁻¹, *P*: 46.7 GPa, IS: 4J; FS: 48N). These positive results suggest that they might be of interest for applications as energetic materials.

Experimental

Caution: although we experienced no difficulties in handling these energetic materials, small scale and best safety practices (leather gloves, face shield) are strongly encouraged. Mechanical actions of these energetic materials involving scratching or scraping must be avoided.

General methods

¹H spectra was recorded on a 300MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer operating at 300 MHz and ¹³C was recorded on a 500MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer operating at 126 MHz. The *d*₆-DMSO and *d*₆-acetone were selected as locking solvents. The decomposition temperatures were determined on a differential scanning calorimeter(DSC823e instrument) at a heating rate of 5 °C min⁻¹. Infrared (IR) spectra were obtained on a Perkin-Elmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 °C. Analyses of C/H/N were performed with a Vario EL III analyzer. Sensitivity towards impact and friction was determined using a BAM friction tester. Densities of the compounds were determined at room temperature by employing a gas pycnometer.

X-ray crystallography

The data for 4, 9, 13, 15 and 16 were collected with a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. A Kryo-Flex low-temperature device was used to keep the crystals at a constant temperature of 173(2) K during the data collection. The data collection and the initial unit cell refinement were performed using APEX2 (v2010.3-0). Data reduction was performed using SAINT (v7.68A) and XPREP (v2008/2). Corrections were applied for Lorentz, polarization, and absorption effects using SADABS (v2008/1). Structures were deduced and refined with the aid of the programs in the SHELXTL-plus (v2008/4) system of programs. The full-matrix least-squares refinement on F2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included in a riding model. The structure was deduced by direct methods with SHELXS-97 and expanded using the Fourier technique. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located and refined.

Syntheses

Synthesis of 4,4'-([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diyl)-bis(1,2,5-oxadiazol-3-nitramide) (4).

Nitric acid (100% 6.0mL) was placed in a 25 mL two-necked round bottom flask and cooled to -10 °C. Compound **3** (0.61 g 2.0 mmol) was slowly added to the cooled nitric acid while maintaining the reaction temperature below -10 °C. The reaction mixture was stirred for 2 hours, then poured into ice water (30.0 mL) and stirred for 1 hour. The precipitate was collected by filtration and washed with ice water and dried at room temperature to give **4** as a colorless solid. Yield 0.58 g (73.73%). T_{d} , 100.8 °C. ¹H NMR (300 MHz, Acetone- d_{6}): δ = 6.80 (s, H) ppm. ¹³C NMR (126 MHz, Acetone- d_{6}): δ = 163.94, 159.31,

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148.22, 141.93 ppm. IR (KBr): 3481, 2747, 1625, 1600, 1516, 1462, 1385, 1308, 1171, 1040, 977, 931, 912, 873, 811 cm⁻¹. Elemental analysis calcd (%) for $C_8H_2N_{12}O_8$ (394.18): C 24.38, H 0.51, N 42.64; found: C 24.62, H 0.55, N 42.53%.

Disilver 4,4'-([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diyl)-bis(1,2,5-oxadiazol-3-nitramide) (5).

Silver nitrate (0.17 g, 1.0 mmol) was dissolved in water (2 mL) and then added to a solution of **4** (0.197 g, 0.5 mmol) in acetonitrile (10 mL). The silver salt precipitated after stirring for 3 h as a light grey powder. The product was filtered to obtain 0.231 g of **5** in a yield of 76.03%.

Diaminoguanidine 4,4'-([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diyl)bis(1,2,5-oxadiazol-3-nitramide) (12)

Salt **5** (0.304 g, 0.5 mmol) was dissolved in acetonitrile (5.0 mL), then guanidinium chloride (0.126 g, 1.0 mmol) was added. Silver chloride started to precipitate immediately and the mixture was filtered warm under exclusion of light. The solution was evaporated to dryness to give 0.253 g of **12** as a light yellow product in a yield of 88.40%. *T*_d, 205.5 °C. ¹H NMR (300 MHz, DMSO-*d*₆): δ = 8.59 (s), 7.17 (s), 4.59 (s) ppm. ¹³C NMR (126 MHz, DMSO-*d*₆): δ = 163.36, 160.64, 159.71, 158.38, 141.41 ppm. IR (KBr): 3424, 3361, 3292, 1684, 1594, 1524, 1498, 1436, 1383, 1300, 1174, 1136, 1041, 1008, 967, 900, 813 cm⁻¹. Elemental analysis calcd (%) for C₁₀H₁₆N₂₂O₈ (572.38): C 20.98, H 2.82, N 53.84; found: C 20.97, H 2.85, N 53.72%.

Triaminoguanidine 4,4'-([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diyl)bis(1,2,5-oxadiazol-3-nitramide) (13).

A similar procedure was followed as that described above for **12**. 0.25 g of **13** as yellowish solid in a yield of 81.65%. T_{d_1} 182.7 °C. ¹H NMR (300 MHz, DMSO- d_6): δ = 8.59 (s), 4.21 (s) ppm. ¹³C NMR (126 MHz, DMSO- d_6): δ = 163.38, 160.66, 159.02, 158.32, 141.43 ppm. IR (KBr): 3338, 3215, 1688, 1586, 1524, 1493, 1425, 1387, 1315, 1272, 1177, 1130, 1004, 966, 932, 897, 809, 538 cm⁻¹. Elemental analysis calcd (%) for C₁₀H₁₈N₂₄O₈ (602.41): C 19.94, H 3.01, N 55.80; found: C 19.92, H 3.02, N 55.81%.

General procedure for the preparation of salts 6-11 and 14-18.

 $\rm NH_3\cdot H_2O$ (1.0 mmol), hydroxylamine solution (1.0 mmol), hydrazine hydrate (1.0 mmol), guanidine carbonate (1.0 mmol), aminoguanidine bicarbonate (1.0 mmol), 1.2,4-triazole (1.0 mmol), 3-amino-1,2,4-triazole (1.0 mmol), 4-amino-1,2,4-triazole (1.0 mmol) and carbohydrazide (1.0 mmol) were added to a solution of 4 (0.197 g, 0.5 mmol) in 5 mL acetonitrile, respectively, and then stirred for 3 h, filtered and dried at room temperature.

Ammonium 4,4'-([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diyl)bis(1,2,5-oxadiazol-3-nitramide) (6)

0.195 g of **6** was obtained in a yield of 91.07%. T_d , 207.2 °C. ¹H NMR (300 MHz, DMSO- d_6): δ = 7.12 (s) ppm; ¹³C NMR (126 MHz, DMSO- d_6): δ = 163.42, 160.67, 158.28, 141.36 ppm; IR (KBr): 3605, 3209, 1598, 1526, 1503, 1438, 1300, 1187, 1139, 1042, 971, 934, 913, 820, 797, 768, 547 cm⁻¹; Elemental analysis calcd (%) for C₈H₈N₁₄O₈ (428.24): C 22.44, H 1.88, N 45.79; found: C 22.45, H 1.89, N 45.75%.

Hydrazinium 4,4'-([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diyl)bis(1,2,5-oxadiazol-3-nitramide) (7)

0.212 g of **7** was obtained in a yield of 92.52%. $T_{\rm d}$, 215.7 °C. ¹H NMR (300 MHz, DMSO- $d_{\rm 6}$): δ = 5.19 (s) ppm; ¹³C NMR (126 MHz, DMSO- $d_{\rm 6}$): δ = 163.52, 160.76, 158.35, 141.48 ppm; IR (KBr): 3406, 3336, 3194, 1661, 1587, 1501, 1432, 1391, 1304, 1097, 969, 874, 823, 770 cm⁻¹; Elemental analysis calcd (%) for C₈H₁₀N₁₆O₈ (458.27): C 20.97, H 2.20, N 48.90; found: C 20.95, H 2.21,N 48.92%.

Hydroxylammonium 4,4'-([5,5'-bi(1,2,4-oxadiazole)]-3,3'diyl)-bis(1,2,5-oxadiazol-3-nitramide) (8)

0.215 g of **8** was obtained in a yield of 93.43%. T_d , 165.3 °C. ¹H NMR (300 MHz, DMSO- d_6): δ = 7.11 (br) ppm; ¹³C NMR (126 MHz, DMSO- d_6): δ = 163.43, 160.69, 158.32, 141.42 ppm; IR (KBr): 3182, 1629, 1524, 1477, 1434, 1371, 1288, 1232, 1177, 1040, 1008, 975, 957, 923, 809, 767 cm⁻¹; Elemental analysis

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calcd (%) for $C_8H_8N_{14}O_{10}$ (460.24): C 20.88, H 1.75, N 42.61; found: C 20.85, H 1.76, N 42.57%.

Didiaminouronium 4,4'-([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diyl)bis(1,2,5-oxadiazol-3-nitramide) (9)

0.254 g of **9** was obtained in a yield of 88.45%. T_d , 209.2 °C. ¹H NMR (300 MHz, DMSO- d_6): $\overline{\delta}$ = 8.43 (br), 3.48 (br) ppm; ¹³C NMR (126 MHz, DMSO- d_6): $\overline{\delta}$ = 163.37, 160.67, 159.19, 158.38, 141.42 ppm; IR (KBr): 3349, 3316, 2938, 2780, 1696, 1628, 1598, 1524, 1425, 1388, 1282, 1176, 1134, 986, 968, 914, 870, 810, 544 cm⁻¹; Elemental analysis calcd (%) for C₁₀H₁₄N₂₀O₁₀ (574.35): C 20.91, H 2.46, N 48.77; found: C 20.88, H 2.31, N 48.77%.

Diaminomethaniminium 4,4'-([5,5'-bi(1,2,4-oxadiazole)]-3,3'diyl)-bis(1,2,5-oxadiazol-3-nitramide) (10)

0.235 g of **10** was obtained in a yield of 91.74%. T_d , 253.1 °C. ¹H NMR (300 MHz, DMSO- d_6): $\bar{\sigma}$ = 6.93 (s) ppm; ¹³C NMR (126 MHz, DMSO- d_6): $\bar{\sigma}$ = 163.48, 160.73, 158.34, 157.98, 141.51 ppm; IR (KBr): 3408, 3344, 3258, 3200, 1661, 1600, 1520, 1499, 1434, 1414, 1300, 1187, 1139, 970, 821, 586 cm⁻¹; Elemental analysis calcd (%) for C₁₀H₁₂N₁₈O₈ (512.32): C 23.44, H 2.36, N 49.21; found: C 23.43, H 2.35,N 49.27%.

Amino(hydrazinyl)methaniminum4,4'-([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diyl)-bis(1,2,5-oxadiazol-3-nitramide) (11)0.242 g of 11 was obtained in a yield of 89.24%. T_d , 211.8 °C.¹H NMR (300 MHz, DMSO- d_6): δ = 8.59 (s), 7.25 (s), 6.79 (s),4.68 (s) ppm; ¹³C NMR (126 MHz, DMSO- d_6): δ = 163.35,160.64, 158.74, 158.35, 141.41 ppm; IR (KBr): 3449, 3311, 1678,1589, 1524, 1498, 1427, 1389, 1300, 1197, 1172, 1132, 1040,968, 920, 874, 821, 769, 545, 499 cm⁻¹; Elemental analysiscalcd (%) for C10H14N20O8 (542.35): C 22.15, H 2.60, N 51.65;found: C 22.12, H 2.61, N 51.67%.

Di(1,2,4-triazolium) 4,4'-([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diyl)bis(1,2,5-oxadiazol-3-nitramide) (14)

0.242 g of **14** was obtained in a yield of 92.05%. T_d , 176.3 °C. ¹H NMR (300 MHz, DMSO- d_6): δ = 10.28 (br), 9.18 (s) ppm; ¹³C NMR (126 MHz, DMSO- d_6): δ = 163.49, 160.42, 157.00, 143.79, 141.53 ppm; IR (KBr): 3102, 2912, 1598, 1553, 1519, 1430, 1400, 1378, 1305, 1254, 1176, 1101, 1040, 970, 940, 913, 882, 852, 826, 628 cm⁻¹; Elemental analysis calcd (%) for C₁₂H₈N₁₈O₈ (532.31): C 27.08, H 1.51, N 47.36; found: C 27.12, H 1.52, N 47.29%.

Di(4-amino-1,2,4-triazolium) 4,4'-([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diyl)-bis(1,2,5-oxadiazol-3-nitramide) (15)

0.259 g of **15** was obtained in a yield of 92.12%. T_d , 219.1 °C. ¹H NMR (300 MHz, DMSO- d_6): δ = 9.47 (s), 8.08 (br) ppm; ¹³C NMR (126 MHz, DMSO- d_6): δ = 163.44, 160.55, 157.72, 144.04, 141.45 ppm; IR (KBr): 3350, 3115, 3026, 1602, 1526, 1497, 1430, 1399, 1275, 1215, 1188, 1139, 1027, 986, 939, 913, 871, 811, 622 cm⁻¹; Elemental analysis calcd (%) for C₁₂H₁₀N₂₀O₈ (562.34): C 25.63, H 1.79, N 49.82; found: C 25.63, H 1.74, N 49.85%.

Di(3-amino-1,2,4-triazolium) 4,4'-([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diyl)-bis(1,2,5-oxadiazol-3-nitramide) (16)

0.253 g of **16** was obtained in a yield of 89.98%. T_d , 182.7 °C. ¹H NMR (300 MHz, DMSO- d_6): δ = 8.31 (s), 8.02 (br) ppm; ¹³C NMR (126 MHz, DMSO- d_6): δ = 163.36, 160.65, 158.26, 150.73, 141.04, 139.24 ppm; IR (KBr): 3419, 3308, 3191, 2775, 1697, 1592, 1518, 1498, 1428, 1323, 1253, 1179, 1039, 970, 949, 911, 875, 842, 767, 716 cm⁻¹; Elemental analysis calcd (%) for C₁₂H₁₀N₂₀O₈ (562.34): C 25.63, H 1.79, N 49.82; found: C 25.63, H 1.76, N 49.77%.

Synthesis of 4,4'-([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diyl)-bis(N-(2,2,2-trinitroethyl)-1,2,5-oxadiazol-3-amine) (17)

4,4'-([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diyl)-bis(1,2,5-oxadiazol-3amide) (0.608 g, 2.0 mmol) was dissolved in hydrochloric acid solution (20 mL), 2,2,2-trinitroethanol (0.905 g, 5.0 mmol) was subsequently added into the reaction solution. The reaction mixture was heated to 80 °C and stirred for 8 hours, then extracted with ethyl acetate, After evaporating the solvent, a white solid was obtained, washed with cold water and dried in air. 0.886 g of **17** was obtained in a yield of 70.33%. T_d , 187.7 °C;

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¹H NMR (300 MHz, Acetone-*d*₆): $\bar{\delta}$ = 6.82 (t, *J* = 6.0 Hz, 1H, -NH-), $\bar{\delta}$ = 5.62 (d, *J* = 6.9 Hz, 2H, -CH₂-) ppm; ¹³C NMR (126 MHz, Acetone-*d*₆): $\bar{\delta}$ = 163.46, 160.13, 155.18, 135.95, 125.55, 47.82 ppm; IR (KBr): 3390, 3011, 1602, 1573, 1505, 1421, 1343, 1324, 1300, 1182, 1146, 1023, 978, 947, 910, 866, 810, 788, 588 cm⁻¹; Elemental analysis calcd (%) for C₁₀H₁₄N₂₀O₈ (542.35): C 22.87, H 0.96, N 40.61; found: C 22.52, H 0.95, N 40.50%.

Synthesis of N,N'-([5,5'-bi(1,2,4-oxadiazole)]-3,3'diylbis(1,2,5-oxadiazole-4,3-diyl))-bis(N-(2,2,2trinitroethyl)nitramide) (18)

To a stirred nitration reagent with a mixture of 100% nitric acid (5 mL) and acetic anhydride (5 mL) was added **17** (0.315 g, 0.5 mmol) at -5 °C. The reaction mixture was stirred at 0 °C for 2 hours and poured into ice water (50 mL). A white solid was filtered and washed with cold water immediately. T_d , 151.8 °C; ¹H NMR (300 MHz, Acetone- d_6): δ = 6.66 (s, 2H,-CH₂-); ¹³C NMR (126 MHz, Acetone- d_6): δ = 164.30, 158.76, 151.40, 142.81, 122.81, 53.04 ppm; IR (KBr): 3669, 2988, 2900, 2388, 2347, 2323, 1993, 1584, 1510, 1419, 1333, 1312, 1287, 1176, 1154, 1028, 989, 938, 908, 876, 806, 777, 590 cm⁻¹; Elemental analysis calcd (%) for C₁₀H₁₄N₂₀O₈ (542.35): C 20.01, H 0.56, N 35.00; found: C 20.02, H 0.53, N 34.70%.

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Key words high-energy-density materials • 3,3'-di(1,2,5oxadiazol-3-yl)-5,5'-bi(1,2,4-oxadiazole) • detonation performance • sensitivity • X-ray diffraction

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