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An unexpected method to synthesise 1,2,4-oxadiazolone derivatives: a class of insensitive energetic materials†

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A new and effective method for the preparation of 3-(4-amino-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5(4*H*)-one is presented. In order to develop high energy density materials, compounds **3**, **4** and **6** were synthesized by the simple nitration, oxidation and oxidation coupling reaction of compound **2**. In addition, six energetic salts based on **3** and **4** were synthesized, respectively. Compounds **2–12** were characterized by IR spectroscopy, multinuclear NMR spectroscopy and elemental analysis. The structures of compounds **2**, **4** and **7** were determined by single crystal X-ray diffraction. In addition, the energetic properties of compounds **3–12** including density (1.60–1.88 g cm^{-3}), thermal stability (161.83–315.75 °C), except compound **3** which decomposed at 127.25 °C, and sensitivity were also investigated. The energetic performance (*P*: 22.25–35.81 GPa; *D*: 7749–8892 m s^{-1}) from the experimental densities and calculated heats of formation suggests that many of them have potential applications as energetic materials.

Introduction

With the pressing need for the synthesis of energetic materials that exhibit low toxicity, high performance, and low sensitivity, the search for new energetic compounds that would have practical applications continues.[1] Over the past few decades, nitrogen-rich heterocycles have attracted increasing attention in the field of energetic materials for constructing new energetic compounds due to their relatively high heat of formation, good thermal stability and improved detonation performance.[2]

As an example, five-membered heterocycles containing two carbon atoms, one oxygen atom, and two nitrogen atoms, known as oxadiazoles (Fig. 1a), are of considerable interest in different areas of pesticide chemistry as well as medicinal and energetic materials science.[3] Most studies show that the oxadiazole moiety reveals promising energetic properties.[4] Since the molecular structure determines properties, insight into the oxadiazole structures helps to understand the key factors that determine their thermal stability and detonation properties.[5] There are four isomers of oxadiazole: 1,2,5-oxadiazole (furazan), 1,2,4-oxadiazole, 1,3,4-oxadiazole, and 1,2,3-oxadiazole (Fig. 1a).[6] Among them, 1,2,4-oxadiazole shows a good balance between energy and stability. Therefore, many energetic compounds bearing a 1,2,4-oxadiazole ring and a 1,2,4-oxadiazole-5(4*H*) ring have been reported in recent years.[7]

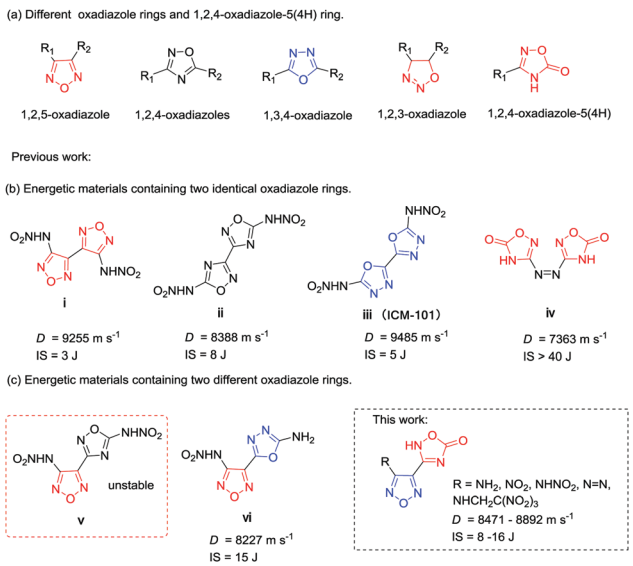

Fig. 1 Oxadiazole rings and some energetic materials containing the same or different oxadiazole rings.

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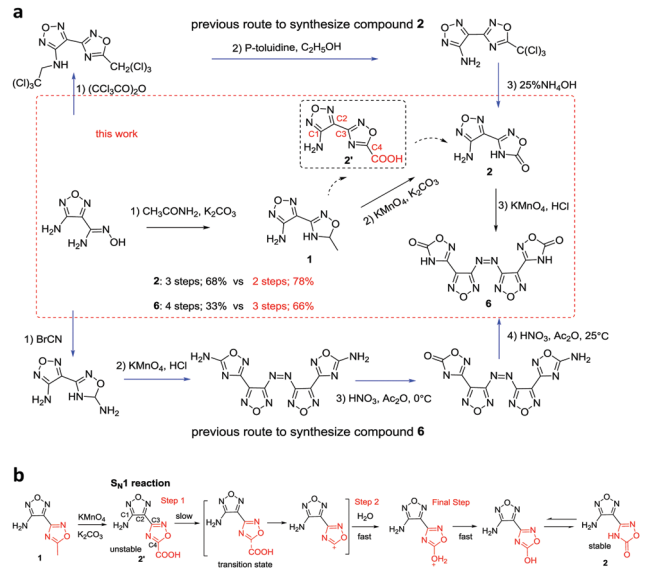


Fig. 2 (a) Different methods to synthesise compounds **2** and **6**. (b) Possible mechanisms for the synthesis of compound **2**.

Over the past decade, a variety of protocols for tuning the properties of energetic materials have been developed.[8] Among them, the introduction of different energetic groups such as $-NO_2$, $-NHNO_2$ and $-N{=}N-$ as substituents on an organic backbone is perhaps the most commonly used method for this purpose. At the same time, in order to make a balance between high performance and low sensitivity, more and more researchers are focusing on combining the same heterocyclic rings into a single molecule to synthesize new high-energy materials. For example, compounds **i** to **iv** which are combined by the same ring all show relatively high detonation performance.[9] Among them, ICM-101 (compound **iii**) shows very impressive properties, including a surprisingly high density of 1.99 g cm^{-3} and excellent detonation performances (D = 9481 m s^{-1}, P = 41.9 GPa), more importantly, it can be prepared through a two-step synthesis from commercially available materials in high yield. In addition, combining the different heterocyclic rings into a single molecule is also an effective strategy to prepare materials with high performance and low sensitivity. For instance, although compound **v** is unstable, the hydroxyammonium salt based on **v** shows not only good detonation performances (P = 37.4 GPa; D = 9046 m s^{-1}) but also good thermal stabilities (T_d = 193 °C).[10] The neutral compound **vi** shows acceptable sensitivity (IS = 15 J, FS = 120 N).[11]

In order to combine the benefits of oxadiazoles, new energetic compounds were synthesized and described herein. We used an unexpected method to synthesize substituted 1,2,4-oxadiazole-5(4*H*)-ones (Fig. 2) and a class of insensitive energetic compounds.

Results and discussion

Syntheses

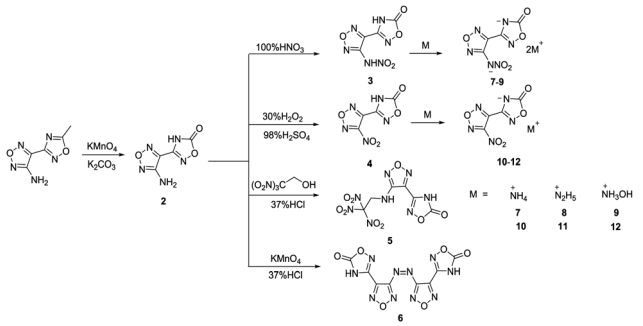
First, 3-amino-4-(5-methyl-1,2,4-oxadiazol-3-yl)furazan (**1**) was synthesized by reacting 4-amino-*N*′-hydroxy-1,2,5-oxadiazole-3-carboximid amide with acetamide according to literature methods.[12]

According to our literature research, the representative methods for the synthesis of substituted 1,2,4-oxadiazole-5(4*H*)-ones(**2** and **6**) have been reported in the literature.[13,14,16] Although these procedures are useful for the construction of 1,2,4-oxadiazole cores, most of them still suffer from some limitations such as the use of toxic and hazardous reagents and laborious reaction procedures with unsatisfactory yields. For example, compound **2** was first presented in 3 steps with a yield of 68% and compound **6** was not only synthesized in 4 steps with a yield of 33%, but also used the toxic and harmful reactant cyanogen bromide (Fig. 2a). Here, we reported a new and effective method for the synthesis of substituted 1,2,4-oxadiazole-5(4*H*)-ones such as the synthesis of compounds **2** and **6**, which make the reaction procedures easier and safer. More importantly, the yields of compounds **2** and **6** increased by about 10% and 33%, respectively.

We originally intended to convert the methyl groups bonded to the 1,2,4-oxadiazole ring to the corresponding carboxylic acid derivative by reacting with oxidation reagents according to the relevant literature.[15] Interestingly, in the presence of two equivalents of $KMnO_4$ in a K_2CO_3 containing water solution, 3-amino-4-(5-methyl-1,2,4-oxadiazol-3-yl)furazan (**1**) was readily converted to 3-(4-amino-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5(4*H*)-one (**2**) when the mixture solution was heated to 100 °C and reacted for 2 hours and no carboxylic acid product formation was observed.

Although the exact mechanism for the synthesis of **2** is not clear yet, a possible mechanism is shown in Fig. 2b. Firstly, the intermediate carboxylic acid product (**2′**) could be formed in the presence of two equivalents of $KMnO_4$. Then the carboxyl group in **2′** was replaced by the hydroxyl group in water through the S_N1 reaction (Fig. 2b), which is supported by the easy leaving group (–COOH) and highly polar water solvent. The S_N1 mechanism is a multistep process. The first step is the formation of a stabilized positive ion taking place in the transition state. The second step is a fast attack on the positive ion by an uncharged water molecule as a nucleophile. Finally, the positively charged product loses a proton to give the uncharged compound **2**.

By treating **2** in 100% nitric acid at 0 °C for 2 h, followed by quenching with ice water, the 3-(4-nitroamine-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5(4*H*)-one (**3**) precipitated in high yield (80.96%). Compound **2** was oxidized with 30% H_2O_2 in concentrated H_2SO_4 to generate 3-(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5(4*H*)-one (**4**) in high yield (85.39%). The *N*-trinitroethyl derivative **5** was synthesized *via* the reactions of the electron-deficient trinitroethanol with the corresponding compound **2** with a yield of 91.37%. *N*-Azo-bridged compounds synthesized by oxidative coupling of $C-NH_2$ groups are well known, and thus compound **6** was formed in a yield of 82%. Due to the presence of acidic hydrogens on the nitroamine or 1,2,4-oxadiazole-5(4*H*)-one ring, **3** and **4** were converted to energetic salts by reacting with different bases in different ratios. When **3** was treated with 2 equiv. of base, monocation energetic salts **7–9** were isolated with an anion/cation ratio of 1 : 2. In contrast, energetic salts **10–12** were obtained by adding 1 equiv. of base (Scheme 1). All the salts were produced in high yield (89.66–92.65%).



Scheme 1 Synthesis of compounds **2–12**.

Spectroscopy

The structures of compounds **2–12** were fully characterized by IR spectroscopy, NMR spectroscopy and elemental analysis. The ^{1}H NMR and ^{13}C NMR spectra of these new compounds are shown in the ESI.†

In the IR spectra, a strong absorption band at 1700 cm^{-1} is attributed to the carbonyl group of the 1,2,4-oxadiazol-5-ones (compounds **2–12**). In the ^{1}H NMR spectrum, for the neutral compounds **2–4**, broad peaks were observed at 6.45–6.70 ppm due to their acidic protons. In the ^{1}H NMR spectrum of **5**, the proton signal of –NH– groups attached to the furazan ring were observed at 7.21 ppm and that of the methylene group was observed at 5.50 ppm. In the ^{13}C NMR spectrum of **2–12**, four signals for furazan and 1,2,4-oxadiazole-5(4*H*)-one ring carbon atoms were found in the expected range. Two singlets for the bridging carbon atoms can be observed at chemical shifts around 139.27 ppm in the ^{13}C NMR spectrum of **6**. The carbon resonance of methylene in compound **5** was found at 47.82 ppm, and the carbon resonance of trinitromethyl was found at 125.73 ppm, which are in good agreement with previously recorded shifts for similar compounds.[17]

X-ray crystallography

Aiming for structural insight, **2**·H_2O, **4**·H_2O and **7** were further characterized by single-crystal X-ray diffraction. Their crystal and structure data are listed in Table 1 and their structures are shown in Fig. 3a and 5a. Selected bond lengths, angles, torsion angles and hydrogen bonds are listed in the ESI† (Tables S2–S10).

2·H_2O crystallized from water as a monohydrate in the monoclinic space group $P2_1/c$, with a density of 1.726 g cm^{-3} at 172 K. As can be seen from Fig. 3a, compound **2** has a nearly planar structure, which is supported by the dihedral angles: N5–C3–C4–C1 1.0(4)°, N1–C1–C4–C3 5.4(4)°, O1–N1–C1–C4 −178.8(2)°, N1–O1–C2–O3 179.5(2)°. As expected, all hydrogen atoms of the molecule participate in hydrogen bonds, the hydrogen atoms form intramolecular and intermolecular hydrogen-bond pairings with neighboring nitrogen and oxygen atoms (N2–H2A···O4 1.94(3) Å, N5–H5A···O1 2.56(3) Å, N5–H5A···O3 1.97(3) Å, N5–H5B···N1 2.36(3) Å and so on) (Fig. 3c). These intensive hydrogen bonding interactions make the packing structure of compound **2** show a wave-like arrangement (Fig. 3b).

Table 1 Crystallographic data for **2**·H_2O, **4**·H_2O and **7**

Crystal	**2**·H_2O	**4**·H_2O	**7**
Formula	$C_5H_5N_5O_4$	$C_4H_3N_5O_6$	$C_4H_8N_8O_5$
Formula weight	187.13	217.11	248.18
Temperature (K)	172(2)	173(2)	173(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	*Pbca*	$P2_1/c$
Volume [Å^3]	720.13(14)	1610.9(2)	971.8(2)
a [Å]	8.6418(10)	8.7552(8)	8.9160(13)
b [Å]	4.9850(5)	8.1840(6)	13.4685(15)
c [Å]	17.235(2)	22.4827(17)	8.1632(12)
α [°]	90	90	90
β [°]	104.095(3)	90	90.542(5)
γ [°]	90	90	90
Z	4	8	4
ρ (calc.) [g cm^{-3}]	1.726	1.790	1.696
F^2	1.048	1.059	1.056
R_1, wR_2 [all data]	0.0754, 0.0930	0.0799, 0.0974	0.1343, 0.1176
R_1, wR_2 [$I \geq 2\sigma(I)$]	0.0431, 0.0821	0.0433, 0.0835	0.0597, 0.0959
CCDC	1834718	1854762	1834720

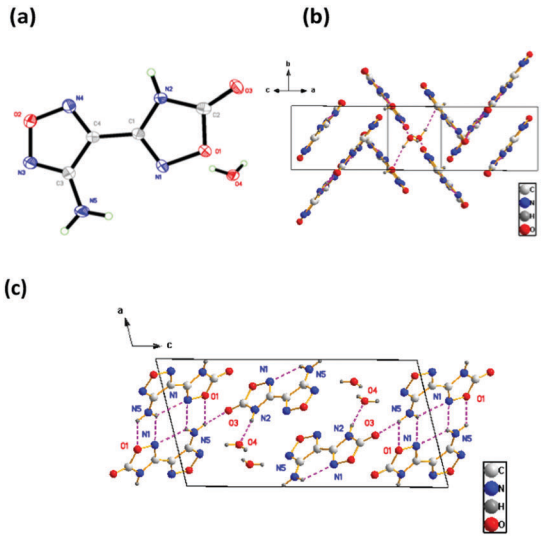


Fig. 3 (a) Single-crystal X-ray structure of **2**·H_2O; (b) criss-cross crystal packing for **2**·H_2O; and (c) hydrogen bonds in **2**·H_2O.

X-ray-quality crystals of **4**·H_2O were obtained by slow evaporation of its aqueous solution. It crystallized in the orthorhombic space group *Pbca* with a density of 1.790 g cm^{-3} at 173 K (Fig. 4a). The C1–N3 bond length is slightly longer than that of compound **2** owing to the strong electron withdrawing nature of the nitro group. Different from compound **2**, the 1,2,4-oxadiazole-5(4*H*)-one ring and furazan ring as well as the nitro group are not in a planar arrangement, which is reflected in the torsion angles (C1–C2–C3–N5 163.54(3) Å, N2–C2–C3–N4 165.39(3) Å, O2–N3–C1–C2 −152.58(3) Å, and O3–N3–C1–N1 −151.58(3) Å). Two kinds of hydrogen bonds can be observed from Fig. 4b. The intermolecular hydrogen-bond formed by hydrogen atoms in the 1,2,4-oxadiazole-5(4*H*)-one rings and the neighboring oxygen atoms in solvent water molecules makes an important contribution to the enhancement of the density of **4**.

The unit cell of **7** crystallizes with a calculated density (1.696 g cm^{-3} at 173 K) in the monoclinic space group $P2_1/c$

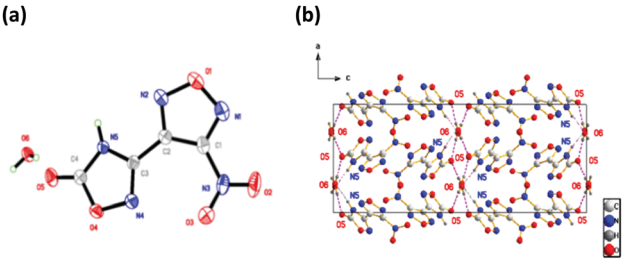


Fig. 4 (a) Single-crystal X-ray structure of **4**·H_2O and (b) hydrogen bonds in **4**·H_2O.

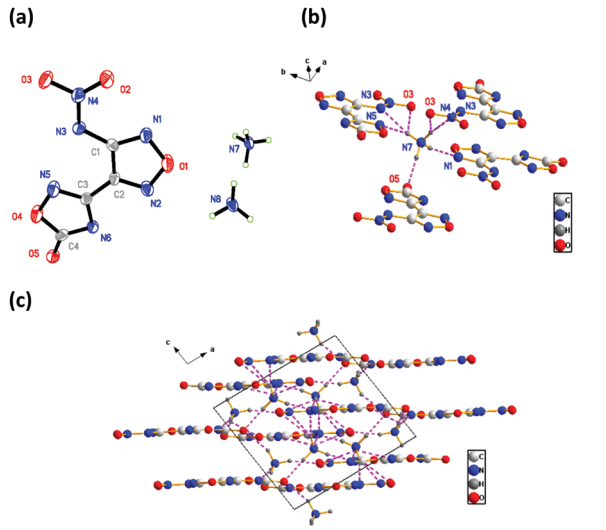


Fig. 5 (a) Single-crystal X-ray structure of **7**; (b) hydrogen bonds in **7**; and (c) layer assembly and the face-to-face crystal packing for **7**.

(Fig. 5a). The bicyclic bridge C3–C2 (1.462(4) Å) is slightly longer than that in **2**·H_2O at 1.449(3) Å (C4–C1). The nitramino groups in the dianion are nearly in the same plane as the oxadiazole rings as indicated by the torsion angles (C1–C2–C3–N6 176.0(3)°, N4–N3–C1–C2 179.1(3)°, C1–N3–N4–O2 −1.5(5)°, and C1–N3–N4–O3 179.0(3)°). In Fig. 5b, intermolecular hydrogen bonds (N7–H7···N3 2.201(18) Å, N7–H7···N5 2.47(2) Å, N7–H7···O5 1.883(18) Å, N7–H7···O3 2.498(18) Å, N7–H7···N4 2.62(2) Å...) are observed. The interlayers of the structure are connected *via* the H-bonds to form a face-to-face stacking (Fig. 5c).

Energetic material properties

The thermal stabilities of these new energetic compounds were examined using differential scanning calorimetric (DSC) measurements in the temperature range from 50 to 350 °C at a heating rate of 5 °C min^{-1}, the decomposition temperatures are given as onset temperatures in Table 2. While neutral compound **3** decomposes thermally at 127.25 °C, its salts (**7–9**) are more thermally stable with decomposition temperatures ranging from 183.75 to 211.51 °C. Compound **6** possesses the highest thermal stability up to 315.75 °C close to that of TNT (T_d = 290 °C). Compound **4** and its salts **10–12** all have relatively high thermal stabilities (192.42–229.75 °C).

The heats of formation of neutral compounds as well as the anions of **3** and **4** were obtained theoretically by using the isodesmic reaction method. The heats of formation of salts **7–12** were calculated based on the Born–Harber energy cycle. The heats of formation of all neutral compounds **3–6** (218.43–611.40 kJ mol^{-1}, 0.66–1.83 kJ g^{-1}) are greater than that of currently used explosive RDX (70.3 kJ mol^{-1}, 0.32 kJ g^{-1}).

As one of the important parameters in the calculation of energetic performance, densities of all new compounds were measured by using a gas pycnometer at 25 °C (Table 2) and found to fall in the range of 1.59–1.88 g cm^{-3}. Among them, neutral compounds **3–6** (1.80–1.88 g cm^{-3}) have relatively high densities that are comparable to that of RDX (1.80 g cm^{-3}). 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 **3–12** were calculated using the EXPLO5 v6.01 program.[18] The calculated detonation velocities and pressures are in the range from 7749 to 8892 m s^{-1} and 22.25 to 35.81 GPa, respectively. Of these compounds, the energetic performance of **5** (D: 8892 m s^{-1}; P: 35.81 GPa) is comparable to that of RDX (D: 8795 m s^{-1}; P: 34.9 GPa).

Impact and friction sensitivities (IS and FS) are high priorities for secondary explosives. Having low friction and impact

Table 2 The physicochemical properties of **3–12** compared with 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX)

Compounds	T_d[a] [°C]	ρ[b] [g cm^{-3}]	ΔH_f[c] [kJ mol^{-1}]/[kJ g^{-1}]	D[d] [m s^{-1}]	P[e] [GPa]	IS[f] [J]	FS[g] [N]
3	127.25	1.83	245.17/1.15	8644	32.50	15	240
4	221.68	1.80	222.79/1.12	8637	32.23	16	240
5	161.83	1.89	218.43/0.66	8892	35.81	8	240
6	315.75	1.86	611.40/1.83	8471	30.20	16	240
7	211.51	1.64	−94.09/−0.44	7749	22.25	>40	>360
8	190.42	1.61	284.21/1.02	8067	26.07	>40	>360
9	183.75	1.68	51.57/0.18	8283	28.33	>40	>360
10	201.92	1.68	152.39/0.71	8031	26.57	>40	>360
11	192.42	1.71	300.95/1.30	8352	29.09	>40	>360
12	229.75	1.76	192.57/0.83	8494	31.74	>40	>360
TNT[h]	295	1.65	−67.0/−0.30	6881	19.5	15	358
RDX[i]	204	1.80	70.3/0.32	8795	34.9	7.5	120

[a] Decomposition temperature from DSC (5 °C min^{-1}). [b] Density measured using a gas pycnometer (25 °C). [c] Calculated molar enthalpy of formation. [d] Calculated detonation velocity. [e] Calculated detonation pressure. [f] Impact sensitivity. [g] Friction sensitivity. [h] Ref. 9. [i] Ref. 4*a*.

sensitivity can greatly improve the safety factor of the weapon during manufacturing and application. The IS and FS values of **3–12** are measured and evaluated by using the standard BAM method,[19] as shown in Table 2. Compounds **3** and **4** have a relatively low impact sensitivity and friction sensitivity (**3**: IS = 15 J, FS = 240 N; **4**: IS = 16 J, FS = 240 N). In addition, most of the energetic salts are very insensitive with IS $>$ 40 J and FS $>$ 360 N.

Conclusions

In summary, we used a new and effective method to synthesize 3-(4-amino-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5(4*H*)-one(**2**). Explosophore groups such as NO_2NH–, NO_2–, $C(NO_2)_3$-CH_2NH– and –N$=$N– were incorporated by a variety of functionalization strategies. Finally, some energetic salts based on **3** and **4** were also synthesized. Compounds **3–12** were also characterized with respect to impact sensitivity, friction sensitivity, and thermal stability. In addition, the structures of **2**·H_2O, **4**·H_2O and **7** were further confirmed by single crystal X-ray diffraction analysis. Most of the energetic salts have adequately acceptable sensitivities (IS $>$ 40 J, FS $>$ 360 N) and attractive detonation properties (D = 7749–8790 m s^{-1}; P = 22.3–32.8 GPa). The neutral compounds **3–5** exhibit good detonation performances (D = 8637–8892 m s^{-1}; P = 32.23–35.81 GPa) which are close to the values of RDX (D = 8795 m s^{-1}; P = 34.9 GPa). It is worth pointing out that compound **6** was not only synthesized in high yield, but also has a high thermal decomposition temperature of 315.75 °C. In addition, the impact sensitivities of neutral compounds **3** and **4** (**3**: IS = 15 J; **4**: IS = 16 J) are similar to that of TNT (IS = 15 J), which suggests that they might be of interest for future applications as environmentally friendly insensitive energetic materials.

Experimental

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

General methods

^{1}H spectra were recorded on a 300MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer operating at 300 MHz and the ^{13}C spectra were recorded on a 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer operating at 126 MHz. 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. The densities of the compounds were determined at room temperature by employing a gas pycnometer.

X-ray crystallography

The data for **2**·H_2O, **4**·H_2O and **7** 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 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 3-(4-amino-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5(4*H*)-one (2). A solution of 3-amino-4-(5-methyl-1,2,4-oxadiazol-3-yl)furazan (1.67 g, 10.0 mmol), $KMnO_4$ (3.16 g, 20.0 mmol) and K_2CO_3 (1.38 g, 10.0 mmol) in 50 mL of water was stirred at 100 °C for 2.5 h. The reaction mixture was cooled to room temperature and the right amount of hydrochloric acid (5.0 mL) was added, then it was extracted with ethyl acetate (3 × 15 mL), and the organic phase was dried with magnesium sulfate and the solvent was evaporated to obtain 1.38 g of **2** as a yellowish solid in a yield of 81.65%. ^{1}H NMR (300 MHz, acetone-d_6): δ = 6.46 (s, H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ = 158.98, 154.76, 149.35, 134.91 ppm. IR (KBr): 3604, 3461, 3322, 3158, 3087, 2929, 2795, 2655, 2477, 2155, 1983, 1935, 1828, 1769, 1694, 1635, 1563, 1474, 1418, 1331, 1239, 1188, 1129, 1010, 953, 906, 858, 721, 647, 567, 442 cm^{-1}. Elemental analysis calcd (%) for $C_4H_3N_5O_3$ (169.10): C 28.41, H 1.79, N 41.42; found: C 28.40, H 1.77, N 41.43%.

Synthesis of *N*-(4-(5-oxo-4,5-dihydro-1,2,4-oxadiazol-3-yl)-1,2,5-oxadiazol-3-yl)nitramide (3). Nitric acid (100%, 6.0 mL) was placed in a 25 mL two-necked round bottom flask and cooled to −10 °C. Compound **2** (0.51 g, 3.0 mmol) was slowly added to the cooled nitric acid while maintaining the reaction temperature below −10 °C. The reaction mixture was stirred for 5 hours, then poured into ice water (50.0 mL) and extracted with ethyl acetate (3 × 15 mL), the organic phase was dried with magnesium sulfate and the solvent was evaporated to obtain 0.52 g of **3** as a yellowish solid in a yield of 80.96%. T_d, 127.25 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 6.70 (s) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ = 159.26, 152.47, 148.48, 140.24 ppm. IR (KBr): 3848, 3744, 3625, 3110, 3069, 2825, 2673, 2310, 2149, 1786, 1563, 1382, 1236, 1185, 1138, 1022, 941, 894, 831, 754, 596, 507, 438 cm^{-1}.

Elemental analysis calcd (%) for $C_4H_2N_6O_5$ (214.10): C 22.44, H 0.94, N 39.25; found: C 22.42, H 0.95, N 39.22%.

Synthesis of 3-(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5(4*H*)-one (4). Compound **2** (0.51 g, 3.0 mmol) was added slowly to a mixture of 30% H_2O_2 (6 mL) and 98% H_2SO_4 (12 mL) with stirring and cooling in an ice bath. After 12 h of reaction at room temperature, the reaction mixture was poured into cold water (35 mL) and extracted with ethyl acetate (3 × 15 mL), the organic phase was dried with magnesium sulfate and the solvent was evaporated under vacuum to give 0.51 g of **4** as a light yellow product in a yield of 85.39%. T_d, 221.68 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 6.45 (s) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ = 165.50, 158.81, 146.35, 138.17 ppm. IR (KBr): 3506, 3298, 3012, 2932, 2840, 2768, 2688, 2548, 2381, 1995, 1789, 1647, 1575, 1528, 1432, 1361, 1251, 1120, 1037, 998, 947, 885, 825, 757, 692, 614, 540, 462 cm^{-1}. Elemental analysis calcd (%) for $C_4H_1N_5O_5$ (199.08): C 24.13, H 0.51, N 35.18; found: C 24.11, H 0.50, N 35.16%.

Synthesis of 3-(4-((2,2,2-trinitroethyl)amino)-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5(4*H*)-one (5). Compound **2** (0.51 g, 3.0 mmol) was dissolved in hydrochloric acid solution (20 mL), and 2,2,2-trinitroethanol (1.09 g, 6.0 mmol) was subsequently added into the reaction solution. The reaction mixture was heated to 100 °C and stirred for 12 hours, and the precipitate was filtered off, washed with water and dried in air to afford **5** (0.91 g) in a yield of 91.37%. T_d, 161.83 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.21 (t, J =5.5 Hz, 1H, –NH–), 5.50 (d, J = 6.1 Hz, 2H, –CH_2–) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 158.83, 154.68, 148.96, 135.01, 125.73, 47.82 ppm; IR (KBr): 3741, 3375, 3137, 1781, 1593, 1388, 1299, 1150, 1022, 947, 944, 805, 742, 653, 596, 543 cm^{-1}; elemental analysis calcd (%) for $C_6H_4N_8O_9$ (332.15): C 21.70, H 1.21, N 33.74; found: C 21.71, H 1.22, N 33.76%.

Synthesis of (*Z*)-3,3′-(diazene-1,2-diylbis(1,2,5-oxadiazole-4,3-diyl))bis(1,2,4-oxadiazol-5(4*H*)-one) (6). To a solution of compound **2** (0.51 g, 3.0 mmol) in 25 mL 37% hydrochloric acid was added a solution of $KMnO_4$ (0.66 g, 4.2 mmol). The reaction mixture was kept for 3 h at 50 °C and treated with 30% hydrogen peroxide, and the precipitate was filtered off, washed with water and dried in air to afford **6** (0.41 g) in a yield of 82.00%. T_d, 315.75 °C. ^{1}H NMR (300 MHz, DMSO-d_6): no signal; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 161.51, 158.88, 147.64, 139.27 ppm; IR (KBr): 3741, 3459, 3078, 3006, 2825, 2712, 1986, 1932, 1816, 1766, 1620, 1545, 1435, 1316, 1245, 1144, 1034, 950, 757, 698, 608, 534 cm^{-1}; elemental analysis calcd (%) for $C_8H_2N_{10}O_6$ (334.17): C 28.75, H 0.60, N 41.92; found: C 28.72, H 0.59, N 41.91%.

General procedure for the preparation of salts 7–9

A solution of aqueous ammonia (0.05 g, 2.75 mmol, 2 : 1 ratio), hydrazine monohydride (0.09 g, 2.75 mmol, 2 : 1 ratio), and hydroxylamine (0.09 g, 2.75 mmol, 2 : 1 ratio) was slowly added to a solution of **3** (0.29 g, 1.37 mmol) in acetonitrile (10 mL) at 25 °C with stirring. After stirring for 1 h at room temperature, the precipitate was filtered off, washed with acetonitrile, and dried in air.

Diammonium *N*-(4-(5-oxo-4,5-dihydro-1,2,4-oxadiazol-3-yl)-1,2,5-oxadiazol-3-yl)nitramide (7)

0.21 g of **7** was obtained in a yield of 90.85%. T_d, 211.51 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.31 (br) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 172.92, 158.83, 157.28, 144.38 ppm; IR (KBr): 3741, 3194, 3090, 2887, 2798, 1694, 1641, 1498, 1432, 1388, 1337, 1287, 1221, 909, 867, 814, 780, 733, 590, 459 cm^{-1}; elemental analysis calcd (%) for $C_4H_8N_8O_5$ (248.16): C 19.36, H 3.25, N 45.15; found: C 19.33, H 3.26, N 45.13%.

Dihydrazium *N*-(4-(5-oxo-4,5-dihydro-1,2,4-oxadiazol-3-yl)-1,2,5-oxadiazol-3-yl)nitramide (8)

0.34 g of **8** was obtained in a yield of 90.67%. T_d, 190.42 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 6.41 (br) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 173.06, 158.70, 157.24, 144.01 ppm; IR (KBr): 3741, 3435, 3310, 3096, 2634, 2202, 1691, 1584, 1510, 1426, 1400, 1313, 1221, 1182, 1108, 971, 909, 825, 775, 596, 445 cm^{-1}; elemental analysis calcd (%) for $C_4H_{10}N_{10}O_5$ (278.19): C 17.27, H 3.62, N 50.35; found: C 17.24, H 3.61, N 50.37%.

Dihydroxylammonium *N*-(4-(5-oxo-4,5-dihydro-1,2,4-oxadiazol-3-yl)-1,2,5-oxadiazol-3-yl)nitramide (9)

0.34 g of **9** was obtained in a yield of 89.95%. T_d, 183.75 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.74 (br) ppm; ^{13}C NMR (126 MHz, DMSO-d_6): δ = 172.81, 157.25, 156.48, 142.96 ppm; IR (KBr): 3845, 3738, 3622, 3057, 2744, 2310, 2016, 1691, 1608, 1510, 1435, 1388, 1304, 1239, 1197, 1010, 924, 879, 828, 772, 680, 599, 507, 453 cm^{-1}; elemental analysis calcd (%) for $C_4H_8N_8O_7$ (280.16): C 17.15, H 2.88, N 40.00; found: C 17.16, H 2.87, N 39.98%.

General procedure for the preparation of salts 10–12

A solution of aqueous ammonia (0.025 g, 1.37 mmol, 1 : 1 ratio), hydrazine monohydride (0.045 g, 1.37 mmol, 2 : 1 ratio), and hydroxylamine (0.045 g, 1.37 mmol, 1 : 1 ratio) was slowly added to a solution of **4** (0.29 g, 1.37 mmol) in acetonitrile (10 mL) at 25 °C with stirring. After stirring for 1 h at room temperature, the precipitate was filtered off, washed with acetonitrile, and dried in air.

Ammonium 3-(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5(4*H*)-one (10)

0.26 g of **10** was obtained in a yield of 89.66%. T_d, 201.92 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.14 (s) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 172.48, 158.74, 155.85, 142.16 ppm; IR (KBr): 3744, 3453, 3191, 3075, 2664, 2444, 2313, 2123, 1673, 1554, 1483, 1382, 1301, 1221, 1138, 1040, 986, 941, 882, 831, 778, 656, 608 cm^{-1}; elemental analysis calcd (%) for $C_4H_4N_6O_5$ (216.11): C 22.23, H 1.87, N 38.89; found: C 22.22, H 1.88, N 38.90%.

Hydrazium 3-(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5(4*H*)-one (11)

0.29 g of **11** was obtained in a yield of 92.95%. T_d, 192.42 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 5.68 (s) ppm; ^{13}C NMR

(75 MHz, DMSO-d_6): δ = 166.77, 159.08, 154.84, 139.23 ppm; IR (KBr): 3744, 3340, 3191, 3090, 2753, 2652, 2155, 1783, 1679, 1599, 1540, 1486, 1388, 1230, 1180, 1096, 1016, 968, 909, 778, 608, 445 cm^{-1}; elemental analysis calcd (%) for $C_4H_5N_7O_5$ (231.13): C 20.79, H 2.18, N 42.42; found: C 20.76, H 2.19, N 42.40%.

Hydroxylammonium 3-(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5(4*H*)-one (12)

0.29 g of **12** was obtained in a yield of 92.65%. T_d, 229.75 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 5.31 (s) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 161.98, 159.23, 148.29, 135.88 ppm; IR (KBr): 3741, 3748, 3476, 3158, 3116, 2834, 2637, 2542, 2149, 1795, 1756, 1703, 1629, 1569, 1447, 1388, 1307, 1236, 1144, 1028, 941, 899, 820, 751, 590, 531 cm^{-1}; elemental analysis calcd (%) for $C_4H_4N_6O_6$ (232.11): C 20.70, H 1.74, N 36.21; found: C 20.68, H 1.75, N 36.20%.

Conflicts of interest

There are no conflicts to declare.

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