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Preparation and characteristics of 1,2,4-oxadiazole-derived energetic ionic salts with nitrogen-linkages

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A new family of energetic ionic salts containing 1,2,4-oxadiazole ring and amino or triazene linkage were synthesized by oxidation of 3-nitro-5-amino-1,2,4-oxadiazole (**NOA**) with sodium dichloroisocyanurate (SDCI) affording sodium bis(3-nitro-1,2,4-oxadiazol-5-yl)triaz-2-en-1-ide (**3**) followed by a cation metathesis. Their molecular structures were fully characterized by ¹H and ¹³C NMR, MS and IR spectra, while three ionic salts **4**, **5** and **7** along with two sodium salt precursors **2** and **3** were confirmed by single crystal X-ray diffraction. Differential scanning calorimetry (DSC) was employed to investigate the thermal stability of these ionic salts, revealing moderate onset decomposition temperatures ranging from 166 °C to 249 °C. By a fall hammer test, most salts exhibits low impact sensitivities. Guanidinium bis(3-nitro-1,2,4-oxadiazol-5-yl)amide (**4**) exhibits a good performance with acceptable detonation properties (*D*: 8351 m s⁻¹, *P*: 29.0 GPa), good stability (*T*_d: 241 °C, onset) and low impact sensitivity (*IS* >40 J).

Introduction

Owing to the low volatility, insensitivity, tailored performance and environmental friendliness, energetic ionic salts have recently emerged to meet the challenging demand of new energetic materials and become one of the most promising and active research topics of high-energy density materials (HEDMs).^[1] They inherit the novel performance properties of original conventional energetic moieties and could be readily modified and optimized through the sagacious combination of different cations and anions which make them extremely promising candidates for existing energetic materials for civilian or military applications. Energetic ionic salts based on pyrazole,^[2] imidazole,^[3] triazole,^[4] tetrazole,^[5] and concomitantly fused heterocyclic derivatives^[6] have attracted widespread attentions and achieved impressive progress in last decades. Ionization of acidic N-H in heterocyclic rings is an effective synthetic transformation to construct versatile energetic molecular architectures. In contrast to azole moieties which could be deprotonated readily to generate target ions, neutral heteroaromatic rings such as oxadiazole, triazine and tetrazine could hardly become a part of energetic fragment as absence of acidic N-H. A promising strategy to solve the problematic non-ionic nitrogen-rich heterocyclic moieties is to be

functionalized by hydroxyl, $^{[2c,5a,7]}$ nitroamine, $^{[3c,8]}$ or dinitromethyl group $^{[4e,9]}$ followed by treatment with a suitable base.

On the other hand, catenated nitrogen chains (e.g., -NH-, -N=N-, -N=N(O)-, -NH-N=N-) have the top priority to be utilized as the energetic linkages because of inherently energetic N–N and N=N bonds leading to high heats of formation and good planarity retention in the target energetic molecules.^[10] Among them, amino (-NH-) and triazene (-NH-N=N-) linkers equipped with a valuable acidic hydrogen would be excellent precursors for energetic ionic salts. To the best of our knowledge, only a few examples of ionic salts bearing amino(-NH-) and triazene (-NH-N=N-) chains have been reported such as dipicrylamine,^[11] bis(methyltetrazolyl)triazene,^[12] and 1,3-bis(4-nitrofurazan-3-yl)triazene,^[13] while the amino (-NH-) bridge of *N*,*N*-bis(1*H*-tetrazol-5-yl)amine failed to be salinized.^[14]

1,2,4-Oxadiazole as an isomer of furazan since the natural superiority of oxygen balance and excellent thermal stability has raised growing attentions in energetic materials.^[15] Our group has focused on 1,2,4-oxadiazole heterocycle for years and great efforts were devoted to develop 1,2,4-oxadiazole-based energetic materials.^[16] To take full advantage of energetic salt and nitrogen chain linkage, amino (-NH-) and triazene (-NH-N=N-) chains were combined with 1,2,4-oxadiazole to develop high-performance and insensitive energetic materials. Herein, we report the synthesis and properties of energetic ionic salts featuring in 1,2,4-oxadiazole core and nitrogen linkages.

Results and discussion

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⁺ Electronic Supplementary Information (ESI) available: details of computation, copies of NMR and IR spectra, DSC curve and single crystal data. CCDC 1565962-1565968. See DOI: 10.1039/x0xx00000x

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Synthesis

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As shown in Scheme 1, the key intermediate 3-nitro-5-amino-1,2,4-oxadiazole (NOA) was prepared by the oxidation of 3,5-(1)^[17] diamino-1,2,4-oxadiazole using $50\%H_2O_2/Na_2WO_4/conc.H_2SO_4$, which was previously synthesized from uric acid after multiple steps.^[16b] Different to the oxidation of its isomer 3,4-diamino-1,2,5-oxadiazole,^[18] oxidation of 1 was much less effective. Even after stubborn optimization of the reaction conditions in recent years in our lab, the oxidation of 1 staggered to a yield of NOA ranging from 8% to 30%, typically around 10%. Further oxidation of NOA with sodium dichloroisocyanurate (SDCI) gave yellow solids sodium bis(3-nitro-1,2,4-oxadiazol-5-yl)amide (2) and sodium 1,3-bis(3-nitro-1,2,4-oxadiazol-5-yl)triaz-2-en-1-ide (3) in 48% and 44% yield, respectively. Subsequently, the metathesis precursors were precipitated from the aqueous solution of silver nitrate and 2 or 3. Treatment of the resulting silver precipitate with guanidinium chloride, diaminoguanidinium chloride. or triaminoguanidinium chloride in methanol afforded amino ionic salts 4-6 and triazenide ionic salts 7-9, respectively.

All compounds were fully characterized by ¹H and ¹³C NMR, MS and IR (see ESI⁺). Single crystals of ionic salts **4**, **5** and **7**, and sodium complexes **2** and **3** were cultivated and analysed by X-ray diffraction. Complex **2** was found in three polymorphs with different solvents.



Scheme 1 Synthesis of energetic ionic salts 4-9.

Crystallography

Crystals of **4** with one molecule of ethyl acetate, **7** with two molecules of **1**,4-dioxane (DIOX), and **5** appropriate for single crystal X-ray diffraction were obtained by slow evaporation of either ethyl acetate, acetonitrile/1,4-dioxane (1:1, V/V), or petroleum ether (PE)/ethyl acetate (2:1, V/V) solution at room temperature. Crystals of sodium intermediates **2** and **3** were recrystallized from ethyl acetate/DIOX solution. Another crystal structure of $2 \cdot 2H_2O$ was achieved from its ethyl acetate solution. A third polymorph of **2'** grew up in unsuccessfully attempting to prepare the hydroxyammonium salt. Their crystallographic data and

As shown in Figure 1, compound **2** crystallizes as a dihydrate in the monoclinic space group $P2_1/n$ with four molecules per unit cell with a calculated density of 1.764 g cm⁻³ at 296 K. The nitrogenbridged 1,2,4-oxadiazole rings and sodium ion exhibit a planar arrangement with slight twist dihedral angles (N(3)-C(3)-N(7)-O(5) 0.27(18)°, N(3)-C(1)-N(1)-C(2) -1.7(2)°, N(1)-C(2)-N(2)-Na(1) 7.6(2)°, N(2)-C(4)-N(6)-O(4) 172.31(12)°). Sodium ion coordinates to N(2) and N(3) atoms from one molecule and N(4) or N(5) atoms from the other to inspire a coplanar layer. Water is approaching to sodium in almost perpendicular direction (O(7)-Na(1)-N(2) 89.10(5)° and O(8)-Na(1)-N(3) 95.61(3)°). The adjacent two layers are connected through a network of hydrogen bonds (O(7)-H(4)-··O(6) 3.26 Å, O(7)-H(3)···O(8) 2.83 Å, O(8)-H(2)···N(4) 2.95 Å, O(8)-H(1)···N(1) 2.92 Å). These intensive hydrogen bonds result in a special face-to-face package with enhanced stability and a higher density.



Figure 1 a) Single crystal structure of 2·2H₂O. b) Ball and stick packing diagram of 2·2H₂O viewed down the *b*-axis. Hydrogen bonds are indicated by dotted lines.

As shown in Figure 2, 1,4-dioxane solvate of **2** alternatively crystallizes in monoclinic space group $P2_1/c$ with eight molecules per unit cell and a lower density of 1.681 g cm⁻³ at 153 K. The bond length of N(3)-C(3) (1.32 Å) is almost equal to that of N(3)-C(2) (1.33 Å) and shorter than normal $C(sp^2)$ -N single bond (formamide, 1.38 Å). It reveals that electrons of nitrogen linkage are delocalized over two 1,2,4-oxadiazole rings forming a large aromatic system. Sodium is surrounded by two anions and two molecules of 1,4-dioxane in a

similar manner with $2 \cdot 2H_2O$ establishing a cross-like arrangement. Interestingly, two molecules of 1,4-dioxane coordinated to the same sodium orientate in different directions. As absence of hydrogen bonding in the crystal, isolated layers contribute to a less density by 0.083 g cm⁻³ than that of $2 \cdot 2H_2O$.

A special polymorph of **2'** was obtained in the presence of hydroxylamine. As shown in Figure 3, sodium complex **2'** crystallizes

in cubic space group *Fd-3* and sixteen molecules in each unit cell. The basic unit consists of seven sodium ions, in which the central one is coordinated with N00G of 1,2,4-oxadiazole rings of six anions in a planar orientation which are outward extended with other six anions through the remaining coordinated six sodium ions, forming a cycle-like structure. The six interior planes are nearly perpendicular to the corresponding exteriors.

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 Table 1 Crystallographic data for 2·2H₂O, 2·DIOX, 2', 3·DIOX, 4·EtOAc, 5, 7·2DIOX

	2 •2H₂O	2.DIOX	2′	3.DIOX	4-EtOAc	5	7 •2DIXO
Formula	$C_4H_4N_7NaO_8$	$C_8H_8N_7NaO_8$	-	$C_8H_8N_9NaO_8$	$C_9H_{14}N_{10}O_8$	$C_5H_8N_{12}O_6$	$C_{11}H_{18}N_{12}O_9$
Mw[g mol ⁻¹]	301.13	353.20	-	381.22	390.30	332.23	462.37
T[K]	296(2)	153(2)	296(2)	296(2)	296(2)	296(2)	296(2)
Crystal size[mm ³]	0.300 × 0.150 × 0.100	0.370 × 0.260 × 0.170	0.300 × 0.150 × 0.100	0.300 × 0.150 × 0.100	0.300 × 0.150 × 0.100	0.300 × 0.150 × 0.100	0.300 × 0.150 × 0.100
Crystal system	Monoclinic	Monoclinic	Cubic	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic
Space group	P21/n	<i>P</i> 2 ₁ /c	F d -3	Pbca	Pbcm	Pna21	<i>P</i> -1
<i>a</i> [Å]	7.8182(4)	18.955(4)	37.2002(12)	9.438(2)	16.141(3)	12.6832(10)	8.9077(8)
<i>b</i> [Å]	12.4042(7)	9.9608(18)	37.2002(12)	34.981(8)	16.706(3)	14.8873(12)	11.0719(10)
<i>c</i> [Å]	12.0228(7)	15.930(3)	37.2002(12)	9.410(2)	6.4305(12)	6.9071(6)	11.9040(10)
<i>α</i> [°]	90	90	90	90	90	90	105.744(3)
<i>в</i> [°]	103.486(2)	111.912(2)	90	90	90	90	95.441(3)
γ[°]	90	90	90	90	90	90	109.541(3)
V[Å ³]	1133.80(11)	2790.5(10)	51480(5)	3106.7(12)	1734.0(6)	1304.19(19)	1042.38(16)
Z	4	8	16	8	4	4	2
ho _{calc} [g cm ⁻³]	1.764	1.681	-	1.630	1.495	1.692	1.473
μ [mm ⁻¹]	0.198	0.175	0.191	0.167	0.131	0.151	0.128
F[000]	608	1440	28305	1552	808	680	480
ϑ range[°]	2.394-31.612	2.350-29.140	1.816-24.992	1.164-28.692	1.754-28.588	2.109-25.480	1.816-28.248
Reflections collected	15228/3497	24352/7478	11343/3797	31927/3879	20473/2390	12555/2429	12831/5143
Index ranges	-11<=h<=11, -17<=k<=17, -16<=l<=17	–25<=h<=25, –13<=k<=9, –21<=l<=21	0<=h<=44, 0<=h<=44, 0<=h<=44,	12<=h<=12, 46<=k<=46, 12<=l<=12	-21<=h<=21, -22<=k<=22, -8<=l<=8	15<=h<=15, 18<=k<=18, 8<=l<=8	-11<=h<=11, -14<=k<=14, -15<=l<=15
R _{int}	0.0208	0.0291	0.0126	0.0550	0.0717	0.0175	0.0173
Data/restraints/parameter	3497/1/181	7478/0/433	3797/0/318	3879/0/235	2390/0/165	2429/1/208	5143/0/289
Final R index[$l > 2\sigma(l)$]	R1 = 0.0363, $wR_2 = 0.0948$	R1 = 0.0485, wR2 = 0.1139	R1 = 0.0489, wR2 = 0.1121	R1 = 0.0762, wR2 = 0.1604	R1 = 0.0546, wR2 = 0.1307	R1 = 0.0292, wR2 = 0.0764	R1 = 0.0549, wR2 = 0.1594
Final R index[all data]	$R_1 = 0.0519,$ w $R_2 = 0.1052$	R1 = 0.0616, wR2 = 0.1217	R1 = 0.0607, wR2 = 0.1193	R1 = 0.1033, wR2 = 0.1719	R1 = 0.0847, wR2 = 0.1486	R1 = 0.0309, wR2 = 0.0775	R1 = 0.0777, wR2 = 0.1793
GOF on F^2	0.998	1.129	1.089	1.105	1.054	1.044	1.049
CCDC	1565962	1565965	1565966	1565968	1565964	1565963	1565967
$R_1 = \sum F_o - F_c / \sum$	$F_{0} _{F_{0}} _{WR_{2}} = [($	$W(F_o^2 - F_c^2)^2)/$	$W(F_o^2)^2]^{1/2}$.				

Figure 4 illustrates **3** with one 1,4-dioxane crystallizing in orthorhombic space group *Pbca* with eight molecules per unit cell and a moderate density of 1.630 g cm⁻³ at 296 K. The bond length of N(1)-N(3) (1.30 Å) and N(1)-N(2) (1.31 Å) are generally equivalent resulting from the average distribution of electrons of the triazene linkage. The whole molecule is nearly planar with torsion angles of almost 180° (N(6)-C(3)-N(8)-O(2) 7.1(5)°, N(6)-C(1)-N(2)-N(1) - 0.1(5)°, N(4)-C(2)-N(3)-Na(1)164.3(3)°, N(4)-C(4)-N(9)-O(3) 0.1(5)°) with exception of 1,4-dioxane. The coordination pattern of **3** resembles that of **2**-DIOX with a slight deviation of 1,4-dioxane

torsion angles. This small change makes $3 \cdot \text{DIOX}$ arranged very regularly in waves when viewed down the *b*-axis. Notably, N(1) atom of triazene bridge is involved in the coordination bond, which is distinct from that of amino(-N-) anion chain of 2.

Compound **4** with one molecule of ethyl acetate crystallizes in orthorhombic space group *Pbcm* with four molecules per unit cell and a low density of 1.495 g cm⁻³ at 296 K (Figure 5). The packing structure of **4** is ideally planar viewed down the *b*-axis without hydrogen bonds between cross layers. However, numerous hydrogen bonding interactions between anions, cations and

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solvents could be clearly identified (Figure 5c). These abundant hydrogen bonds play a significant role in maintaining the flatness and stability of molecular arrangement in one layer. It is notable that the kernel guanidinium cation acts as a versatile hydrogen bond donor connecting two adjacent anions (N(9)-H(9A)...N(5) 2.96 Å, N(8)-H(8B)…O(3) 3.06 Å, N(8)-H(8A)…N(2) 3.26 Å, N(8)-H(8A)…O(4) 3.18 Å, N(10)-H(10B)…N(6) 3.01 Å, N(10)-H(10A)…N(1) 3.06 Å) and one molecule of ethyl acetate (N(9)-H(9B)···O(7) 2.86 Å, N(8)-H(8B)···O(7) 3.23 Å) forming a solid hydrogen bonding network. The length of ((N(9)-H(9B)…O(7) 2.86 Å) is remarkably short than that of other hydrogen bonds making that ethyl acetate could not be easily wiped off in mild conditions. Additional nonclassic hydrogen bonding interactions between cations and solvents (C(6)-H(6C)···O(6) 3.25 Å and C(6)-H(6A)···O(2) 3.42 Å) are also observed. C(1)-N(1) single bond is allowed to rotate freely in favour of the formation of hydrogen bonds between the cation and anion, resulting in the longer bond length of C(1)-N(1) (1.34 Å) than that of the C(2)-N(1) (1.31 Å) in 1,2,4-oxadiazole. The distinction of these two C-N single bonds erode the molecular spatial symmetry and aromaticity.



Figure 2 a) Single crystal structure of 2·DIOX. b) Ball and stick packing diagram of 2·DIOX showing a cross-like arrangement.



Figure 3 Single crystal structure of 2'.



Figure 4 a) Single crystal structure of 3-DIOX. b) Ball and stick packing diagram of 3-DIOX showing the wave-like arrangement viewed down the *b*-axis.

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Figure 5 a) Single crystal structure of **4**·EtOAc. b) Ball and stick packing diagram of **4**·EtOAc viewed down the *b*-axis. c) Hydrogen bonds are indicated by dotted lines viewed down *c*-axis with one layer.

Solvent-free compound **5** that crystallizes in orthorhombic space group $Pna2_1$ with four molecules per unit cell shows a moderate density of 1.692 g cm⁻³ at 296 K (Figure 6). The cation is approximately vertical to the nitrogen-linked 1,2,4-oxadiazole rings, favouring the formation of internal hydrogen bonds (N(11)-H(11)...N(5) 3.17 Å, N(11)-H(11)...N(4) 3.14 Å, N(12)-H(12B)...O(6) 3.35 Å, N(12)-H(12A)...O(4) 3.22 Å). Diaminoguanidinium cation is just like a bridge to connect two layers of anions through diverse intermolecular hydrogen bonds (N(10)-H(10A)...N(2) 3.35 Å, N(9)-H(9)...O(6) 3.10 Å, N(8)-H(8B)...N(5) 3.20 Å, and N(8)-H(8A)...N(1) 3.00 Å) together with intramolecular ones. In comparison with crystal **4**-EtOAc, the planarity of each layer of **5** is bent in favour of the development of hydrogen bonding interactions between two

adjacent layers. As a result, one nitro group is distorted from its plane with torsion angles of around 20° (N(3)-C(4)-N(7)-O(5) -20.6(5)°, and N(5)-C(4)-N(7)-O(6) -21.3(4)°).



Figure 6 a) Single crystal structure of 5. b) Ball and stick packing diagram of 5 viewed down the c-axis. Hydrogen bonds are indicated by dotted lines.

Compound **7** with two molecules of 1,4-dioxane crystallizes in triclinic space group *P*-1 with two molecules per unit cell and a low density of 1.473 g cm⁻³ at 296 K due to solvation (Figure 7). The bond length of N(4)-N(5) (1.30 Å) and N(5)-N(6) (1.31 Å) is consistent with that of **3**·DIOX, indicating that negative charge is delocalized over the triazene (-N-N=N-) anion moiety. Ignorant of solvent, the structure is flat as expected, which is reflected by the torsion angles of nearly 0° or 180° (N(3)-C(1)-N(1)-O(1) 176.4(2)°, N(3)-C(2)-N(4)-N(5) -0.9(3)°, N(4)-N(5)-N(6)-C(3) -179.87(15)°, and N(7)-C(4)-N(9)-O(5) -6.2(3)°). Similar to compound **4**, layers of **7** are parallel to each other without any hydrogen bonds. Interestingly, guanidinium cation is perfectly compatible with 1,3-bis(3-nitro-1,2,4-oxadiazol-5-yl)triazenide anion through intramolecular hydrogen bonds (N(12)-H(12B)···N(7) 3.02 Å, N(12)-H(12A)···N(3)

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3.03 Å, N(11)-H(11B) \cdots O(5) 3.05 Å, and N(10)-H(10A) \cdots O(2) 3.06 Å) and intermolecular ones (N(11)-H(11A) \cdots N(6) 3.03 Å and N(10)-H(10B) \cdots N(4) 3.05 Å). This ingenious hydrogen bonding exhibited in Figure 7c in one layer brings about a perfect planar sheet in the crystal.



Figure 7 a) Single crystal structure of **7**·2DIOX. b) Ball and stick packing diagram of **7**·2DIOX viewed down the *a*-axis. c) Hydrogen bonds are indicated by dotted lines viewed down the *c*-axis with one layer with the omission of solvent.

Physical and energetic properties

Thermal behaviours of compounds **2-9** were investigated by differential scanning calorimetry (DSC) technique scanning at 5 $^{\circ}$ C min⁻¹ under argon atmosphere. As illustrated in Figure 8,

compound **2** shows an acceptable heat-resistant ability decomposing at 252 °C (peak), while compound **3** decomposes at a lower temperature (230 °C, peak) because of the fragility of triazene (-N-N=N-) compared to amino (-N-) linkage. Compared with the precursor sodium salt **2** (or **3**), compounds **4-6** (or **7-9**) possess decreased decomposition temperatures and distinct melting points. The results imply that coordination bonds are superior to hydrogen bonding in enhancing molecule stability. Compounds **6**, **7** and **9** decompose as soon as melt, which is consistent with bis(guanidine)iminobis(5-tetrazolate) (HBTA-G),^[14a] and ammonium bis(2-methyl-tetrazol-5-yl)-triazenate (MTTNE-A).^[12] Gratifyingly, compounds **4**, **5** and **8** have a comparatively wide temperature range between melting and decomposition, and guanidinium salts (**4** and **7**) are as sufficiently thermal stable as RDX as a result of inter- and intramolecular hydrogen bonding.



Figure 8 DSC plots of compounds 2-9.

Oxygen balance (OB) is a significant index to suggest the high performance of energetic materials which is calculated on the basis of carbon monoxide and water as the products. Apart from compound **2** and **3** with positive OB value (Table 2), all salts possess a slight negative oxygen balance value.

Heats of formation of all compound were calculated based on isodesmic reactions by using Gaussian 09 program package (Revision B.01).^[19] As shown in Table 2, the enthalpy of formation ranging from 0.41 KJ g⁻¹ to 2.02 KJ g⁻¹ is higher than that of TNT and comparable to HBTA-G. And it is reasonable to figure out that triazene-based salts have an obvious advantage over amino-based analogues due to the enormous energy release of N-N and N=N bonds.

The densities of compound **2-9** were measured by employing a gas pycnometer (25 °C) with the exception for compound **5**. Compound **2** and **3** possess the highest densities of 1.803 g cm⁻³ and 1.847 g cm⁻³, respectively, while a lower density was found for their guanidinium-series salts ranging from 1.598 g cm⁻³ to 1.799 g cm⁻³. To our delight, compound **4** retains the high density of approximate 1.80 g cm⁻³. However, it is worthy to be noted that triazene-based salts have a sharply decreasing density compared to the nitrogen-linked counterparts **4-6**.

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Detonation parameters were evaluated with EXPLO5 (v6.01) program based on the measured densities and calculated heats of formation. Triguanidinium bis(3-nitro-1,2,4-oxadiazol-5-yl)amide (**6**) exhibits the best detonation properties (*D*: 8542 m s⁻¹, *P*: 29.4 GPa), which are much better than that of HBTA-G and lower than that of RDX. Compound **4** shows a slightly lower performance than **6** with a detonation velocity of 8351 m s⁻¹ and a detonation pressure of 29.0 GPa. With low densities of triazene (-NH-N=N-) linkage, compounds **7-9** illustrate a moderate detonation performance with about 8000 m s⁻¹ detonation velocity and 25 GPa detonation pressure.

Standard drop hammer tests were conducted to determine the impact sensitivities of all salts. All energetic salts are less mechanically sensitive than HBTA-G, MTTNE-A, RDX and TNT. Most are impact-insensitive (IS > 40 J). The results show that the incorporation of 1,2,4-oxadiazole could effectively decrease the sensitivities of energetic materials.

Conclusions

In summary, a new family of energetic salts based on 3-nitro-5amino-1,2,4-oxadiazole (**NOA**) were synthesized and fully characterized. Amino-bridged ionic salts **4-6** demonstrate better detonation performance than triazene-linked counterparts **7-9**. Guanidinium bis(3-nitro-1,2,4-oxadiazol-5yl)amide **(4)** exhibited an outstanding performance with acceptable detonation properties (*D*: 8351 m s⁻¹, *P*: 29.0 GPa), good stability (T_d = 241 °C, onset) and low impact insensitivity (*IS* >40 J).

Conflicts of interest

There	are	no	conflicts	to	declare.

Table 2 Physical and detonation properties of compound 2-3.										
Entry	Compd.	$T_{\rm m}^{[a]}$ [°C]	<i>T</i> _d ^[b] [°C]	$ ho^{[c]}$ [g cm ⁻³]	$\mathcal{Q}^{[d]}$	$\Delta H_{\rm f}^{[\rm e]}$ [kJ mol ⁻¹ /kJ g ⁻¹]	$D^{[{ m f}]}$ [m s ⁻¹]	P ^[g] [GPa]	<i>IS</i> ^[h] [J]	
1	2	-	249	1.803	12.1	126.0/0.48	7701	25.0	20	
2	3	-	227	1.847	10.9	405.2/1.38	8180	29.0	>40	
3	4	187	241	1.799	-10.6	124.0/0.41	8351	29.0	>40	
4	5	149	197	1.692 ^[i]	-14.4	347.3/1.05	8205	26.5	>40	
5	6	155	171	1.741	-16.1	470.7/1.36	8542	29.4	30	
6	7	204	206	1.621	-9.7	416.1/1.26	7894	24.2	>40	
7	8	113	189	1.618	-13.3	628.2/1.74	8084	25.4	>40	
8	9	153	166	1.598	-14.9	758.4/2.02	8118	25.3	25	
9	HBTA-G ^[14a]	259	260	1.52	-61.9	465/1.71	7636	17.5	_	
10	MTTNE-A ^[12]	205	205	1.6	-63.7	647/2.86	8484	24.8	4	
11	TNT	81	295	1.650	-24.7	-67/-0.29	6881	19.5	15	
12	RDX	-	230	1.82	0	92.6/0.42	8997	35.2	7.4	

Table 2 Physical and detonation properties of compound 2-9.

[a] Melting point (peak). [b] Decomposition temperature (onset), (DSC, 5 °C min⁻¹). [c] Density measured using a gas pycnometer (25 °C). [d] Oxygen balance (based on CO) for $C_aH_bN_cO_d$: OB = 1600*(d-a-b/2)/Mw, Mw = molecular weight. [e] Heat of formation (calculated with Gaussian 09 (vB.01)). [f] Detonation velocity (calculated with EXPLO5 (v6.01)). [g] Detonation pressure (calculated with EXPLO5 (v6.01)). [h] Impact sensitivity (BAM methods). [i] Crystal density.

Experimental

Cautions: Although nothing dangerous was encountered in the procedure of preparing these energetic materials, it is extremely necessary to manipulate on a small scale and use proper protective measures always.

Syntheses

Preparation of 3-nitro-5-amino-1,2,4-oxadiazole (1). Na₂WO₄·2H₂O (4.95 g, 15 mmol) was dissolved in 50% H₂O₂ (25 mL) and conc. H_2SO_4 (3 mL) was added dropwise under water bath. Then 3,5-diamino-1,2,4-oxadiazole (5 g, 50 mmol) was added slowly to avoid the vigorous decomposition of H_2O_2 . After stirring for 24 h, the mixture was quenched with adequate water followed by extraction with ethyl acetate three times. Combined organic phases were washed with aqueous sodium bicarbonate and brine, dried over magnesium sulphate and evaporated under reduced pressure to obtain the crude product. After purification by column chromatography

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(PE/EtOAc = 2:1, V/V), a pure white solid was obtained with the yield around 10%.

Preparation of sodium bis(3-nitro-1,2,4-oxadiazol-5yl)amide (2) and sodium 1,3-bis(3-nitro-1,2,4-oxadiazol-5yl)triaz-2-en-1-ide (3). SDCI (880 mg, 4 mmol) was dissolved in water (50 mL) and a catalytic amount of acetic acid (0.2 mL) was added to activate at 35 °C for 1 h. Then 1 was carefully added to the solution and stirred for another 3 h. The reaction mixture was poured into ice water and extracted with ethyl acetate followed by washing with aqueous sodium bicarbonate. After evaporation of solvent and column chromatography (PE/EtOAc = 2:1, V/V) afforded 2 in 48% and 3 in 44% yield as yellow solid, respectively.

Bis(3-nitro-1,2,4-oxadiazol-5-yl)amide (2). Yellow solid, 254 mg, 48%. *T*_d (onset) = 249 °C. ¹³C NMR (100 MHz, DMSO*d*₆): δ = 174, 170 ppm. IR (KBr pellet): 1564, 1520, 1397, 1295, 1250, 1114, 1079 cm⁻¹. HRMS: calc. for C₄N₇O₆ [M–Na]⁻: 241.9916, found: 241.9918.

1,3-Bis(3-nitro-1,2,4-oxadiazol-5-yl)triazenide (3). Yellow solid, 258 mg, 44%. T_d (onset) = 227 °C. ¹³C NMR (100 MHz, DMSO- d_6): δ = 180, 170 ppm. IR (KBr pellet): 1561, 1478, 1332, 1287, 1223, 1115, 1078 cm⁻¹. HRMS: calc. for C₄N₉O₆ [M–Na]⁻: 269.9977, found: 269.9976.

General procedure for the preparation of the salts (4-9). Sliver nitrate (170 mg, 1 mmol) was dissolved in water (10 mL) and slowly added to a solution of 2 (265 mg, 1 mmol) for 4-6 or 3 (293 mg, 1 mmol) for 7-9 in water (20 mL). The mixture was stirred for 3 h, and a yellow solid was obtained by filtrating and washing with an excess of water. The solid was immersed in MeOH (20 mL) which was added guanidinium chloride, diaminoguanidinium chloride, or triaminoguanidinium chloride with rigorous stirring for another 24 h. The mixture was filtered and the solution was evaporated to remove the solvent. The resulting solid was extracted with ethyl acetate to give a pure yellow solid.

Guanidinium bis(3-nitro-1,2,4-oxadiazol-5-yl)amide (4). Yellow solid, 274 mg, 91%. T_m (peak) = 187 °C, T_d (onset) = 249 °C. ¹H NMR (400 MHz, DMSO- d_6): δ = 6.89(s, 6H) ppm. ¹³C NMR (100 MHz, DMSO- d_6): δ = 174, 170, 158 ppm. IR (KBr pellet): 3508, 3466, 3412, 3342, 3292, 3169, 1664, 1616, 1560, 1521, 1404, 1298, 1232 cm⁻¹.

Diguanidinium bis(3-nitro-1,2,4-oxadiazol-5-yl)amide (5). Yellow solid, 233 mg, 70%. T_m (peak) =149 °C, T_d (onset) = 205 °C. ¹H NMR (400 MHz, DMSO- d_6): δ = 8.53 (s, 2H), 7.13 (s, 2H), 4.58 (s, 4H) ppm. ¹³C NMR (100 MHz, DMSO- d_6): δ = 174, 170, 160 ppm. IR (KBr pellet): 3450, 3385, 3360, 3317, 3173, 1683, 1618, 1603, 1560, 1526, 1402, 1296, 1238 cm⁻¹.

Triguanidinium bis(3-nitro-1,2,4-oxadiazol-5-yl)amide (6). Yellow solid, 253 mg, 73%. T_m (peak) = 155 °C, T_d (onset) = 188°C. ¹H NMR (400 MHz, DMSO- d_6): δ = 8.59 (s, 3H), 4.49 (s, 6H) ppm. ¹³C NMR (100 MHz, DMSO- d_6): δ = 174, 170, 159 ppm. IR (KBr pellet): 3634, 3318, 3210, 1688, 1597, 1566, 1522, 1404, 1302, 1240 cm⁻¹.

Guanidinium 1,3-bis(3-nitro-1,2,4-oxadiazol-5-yl)triaz-2en-1-ide (7). Yellow solid, 284 mg, 86%. T_m (peak) = 204 °C, T_d (onset) = 238 °C. ¹H NMR (400 MHz, DMSO- d_6): δ = 6.70 (s, 6H) ppm. ¹³C NMR (100 MHz, DMSO- d_6): δ = 180, 170, 158 ppm. IR (KBr pellet): 3458, 3356, 3282, 3190, 1682, 1583, 1560, 1506, 1485, 1398, 1323, 1305, 1259 cm⁻¹.

Diguanidinium 1,3-bis(3-nitro-1,2,4-oxadiazol-5-yl)triaz-2-en-1-ide (8). Yellow solid, 270 mg, 75%. *T*_m (peak) = 113 °C, *T*_d (onset) = 195 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 8.54 (s, 2H), 7.14 (s, 2H), 4.59 (s, 4H) ppm. ¹³C NMR (100 MHz, DMSO*d*₆): δ = 180, 170, 160 ppm. IR (KBr pellet): 3485, 3374, 3194, 3122, 1683, 1560, 1491, 1400, 1344, 1269, 1250 cm⁻¹.

Triguanidinium 1,3-bis(3-nitro-1,2,4-oxadiazol-5-yl)triaz-2-en-1-ide (9). Yellow solid, 338 mg, 90%. *T*_m (peak) = 153 °C, *T*_d (onset) = 182 °C. ¹H NMR (400 MHz, DMSO-*d*₆): *δ* = 8.60 (s, 3H), 4.49 (s, 6H) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆): *δ* =180, 170, 160 ppm. IR (KBr pellet): 3317, 3211, 1586, 1555, 1508, 1398, 1275, 1240, 1128 cm⁻¹.

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A new family of nitrogen-bridged energetic ionic salts were synthesized exhibiting good stabilities and low sensitivities.

