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Synthesis and properties of gem-dinitro energetic salts based on 1,2,4-oxadiazole with low impact sensitivity†

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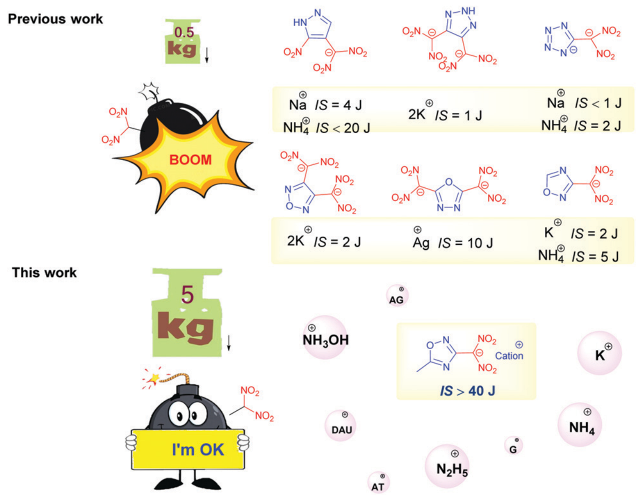
Eight energetic salts with a gem-dinitro group based on 1,2,4-oxadiazole were developed. All of the structures were confirmed by infrared (IR) spectroscopy, ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, and high-resolution mass spectrometry (HRMS), and single-crystal X-ray diffraction was used to determine the structures of the pivotal intermediate 3-(chlorodinitromethyl)-5-methyl-1,2,4-oxadiazole (3), the potassium salt (4) and the hydrazinium salt (7). All of them are insensitive to impact (>40 J) and have higher energy levels than trinitrotoluene (TNT).

As the energy sources for the initial launch of and terminal damage by weapon systems, energetic materials have important military value and strategic significance.[1] In order to improve the efficiency and destruction capabilities of weapons, researchers have focused on developing high-energy materials over the years[2] and have explored two key strategies. Optimization of the molecular structure, especially the planar stacking, is a hot topic in improving the performance.[3] However, a higher number of nitro groups should be incorporated in these materials because of the better detonation properties of nitrogen- and oxygen-rich compositions, such as those of CL-20, which contains six nitro groups, and octanitrocubane (ONC), which has eight nitro groups.[4] A common and more readily accessible strategy is introducing a dinitromethyl group to various backbones, such as 1,3,4-oxadiazole,[5] furoxan,[6] pyrazole,[7] triazole,[8] tetrazole,[9] and 1,2,4-oxadiazole.[10]

However, it is a pity that most gem-dinitro compounds are far from suitable for real applications, even with their attractive energy, as a result of the following notable drawbacks: (a) the acidic hydrogen atom of dinitromethylene leads to hygroscopicity; (b) their ionic salts generally show high sensitivity; (c) some synthetic routes to them are not cost effective. On the contrary, trinitrotoluene (TNT) is deservedly the oldest and most common secondary explosive for multifarious applications owing to its insensitivity to mechanical stimuli.[11] Thus, for application, it is meaningful to reduce the sensitivity of gem-dinitro compounds while at the same time maintaining a higher energy level than TNT.

Our group has been working on high-energy insensitive materials for over ten years[12] and we first reported an insensitive explosive based on 1,2,4-oxadiazole.[13] Follow-up studies have proved that the 1,2,4-oxadiazole ring is an insensitive energetic backbone,[14] which encouraged us to still choose 1,2,4-oxadiazole as the energetic backbone. In this work, we successfully constructed insensitive gem-dinitro derivatives based on 1,2,4-oxadiazole (Scheme 1).



Scheme 1 Previous energetic materials with gem-dinitro groups and this work.

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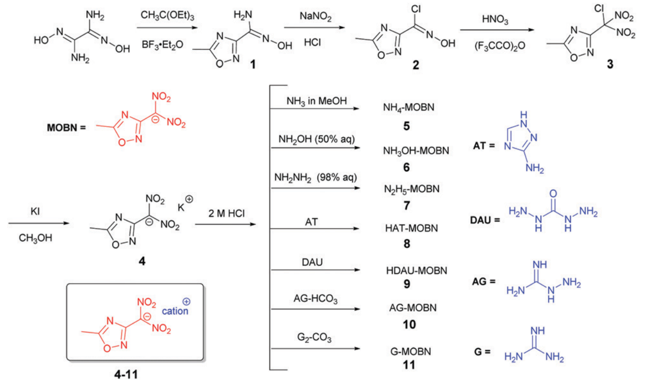

Scheme 2 Synthetic routes for compounds **1–11**.

The synthetic routes for compounds **1–11** are shown in Scheme 2. The initial reactant diaminoglyoxime was synthesized according to the literature.[15] N'-Hydroxy-3-carboximidamide-5-methyl-1,2,4-oxadiazole (**1**) was prepared by cyclization with triethyl orthoacetate under the catalysis of $BF_3{\cdot}Et_2O$ giving a white solid in 93% yield, following a reported procedure.[16] After diazotization and chlorination of **1**, 3-carbimidoyl chloride-5-methyl-1,2,4-oxadiazole (**2**) was obtained in a yield of 85%. Direct nitration of **2** with fuming HNO_3 and trifluoroacetic acid anhydride $(CF_3CO)_2O$ produced gem-dinitro-containing 3-(chlorodinitromethyl)-5-methyl-1,2,4-oxadiazole (**3**) as a white solid in a moderate yield of 43% with the optimal reaction time of 8 h (see the ESI†). Significantly, we obtained a single crystal of **3** for X-ray diffraction, which has been rarely reported in analogical works and usually the nitration product of chloroxime was used directly as an intermediate without any further characterization.[6–10] Potassium (5-methyl-1,2,4-oxadiazol-3-yl)dinitromethanide (**4**) was easily prepared by the treatment of **3** with KI in methanol, with a yield of 85%. Subsequently, **4** was acidified by 2 M HCl and extracted with ethyl acetate to obtain a yellow oil, which was put into ammonium in methanol to afford a yellow solid that was identified as ammonium (5-methyl-1,2,4-oxadiazol-3-yl)-dinitromethanide (**5**), to give a yield of 81%. Similarly, the ionic salts **6–9** were also derived from **4** using the corresponding nitrogen-rich bases (hydroxylamine, hydrazine, 3-amino-1,2,4-triazole, carbohydrazide) in methanol by taking advantage of the difference in acidity while aminoguanidinium (**10**) and guanidinium (**11**) were synthesized from aminoguanidine bicarbonate and guanidine carbonate, respectively, with the release of carbon dioxide facilitating the reaction. The yields of the above reactions were between 65 and 86%.

All compounds were characterized by FT-IR and ^1H and ^{13}C NMR spectroscopy together with HRMS (see the ESI†). A single crystal of **3** suitable for X-ray diffraction was obtained for the first time by dissolving it in a mixture of petroleum ether (PE) and ethyl acetate (EtOAc) and evaporating slowly at 4 °C while single crystals of compounds **4** and **7** were obtained by slow evaporation of **4** and **7** in MeOH/H_2O at ambient temperature. The selected data and structure refinement details of the crystals are presented in the ESI.†

The structure of the vital intermediate **3** is shown in Fig. 1a and it crystallizes in the monoclinic space group $P21/c$ with a crystal density of 1.799 g cm^{-3} at 296 K (CCDC 2018730†). The plane of N(3)–N(4)–Cl(1) and the plane of oxadiazole are almost perpendicular, with a dihedral angle of 88.56°, which leads to a cross 1D structure.[17] Generally, a planar configuration is expected to give a better density, but to our surprise, **3** still has a better density of 1.799 g cm^{-3} compared to other compounds owing to its more compact stacking structure *via* head-to-tail assembly. This special head-to-tail assembly not only economizes space to improve density but also facilitates more hydrogen bonds between the methyl group (head) and the oxygen of the NO_2 group (tail), which greatly reduces the sensitivity (Fig. 1b).[18] As expected, the impact sensitivity of **3** is over 40 J.

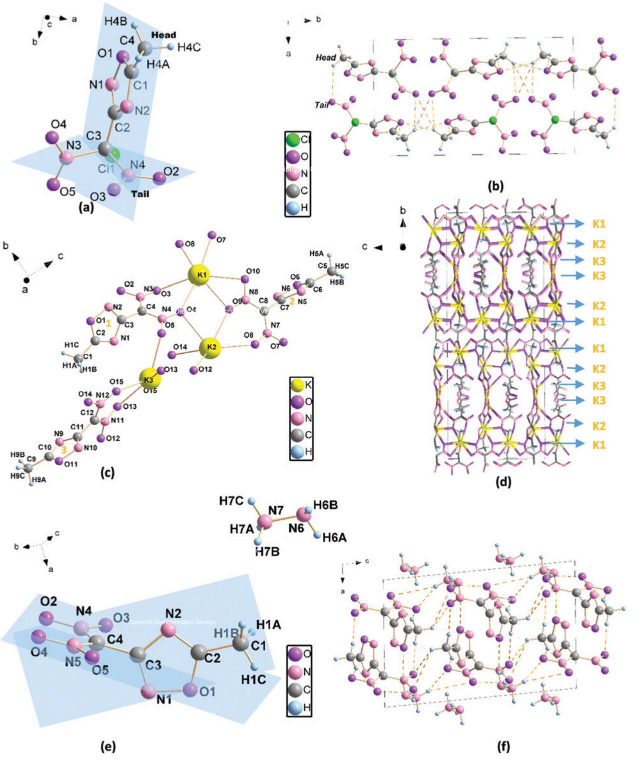

Fig. 1 (a) X-ray crystal structure of **3**; (b) packing diagram of **3**; (c) X-ray crystal structure of **4**; (d) packing diagram of **4**; (e) X-ray crystal structure of **7**; and (f) packing diagram of **7**.

The potassium salt of **4** crystallizes in the orthorhombic space group $Pbca$ with a density of 1.864 g cm^{-3} based on crystal data (CCDC 2038764†). It is worth pointing out that the K atoms have three different coordination modes. In Fig. 1c, K(1) is chelated by six oxygen atoms while K(2) and K(3) are chelated by five oxygen atoms. The average K–O distance is 2.77 Å, which is shorter than those in previous reports,[19] especially K(3)–O, which is just 2.75 Å. In turn, there are also three types of 1,2,4-oxadiazole, whose dihedral angles with the plane of dinitromethylene are 71.19°, 80.00° and 51.05°, respectively. Thus, an interesting three-dimensional metal–organic framework (3D MOF) was formed, as presented in Fig. 1d, and different parallels were formed by the ordered coordination of different potassium atoms in the a-axis.

Table 1 Physical properties and detonation performance of **3–11**

Compd.	$T_d{}^a$ [°C]	ρ^b [g cm^{-3}]	ΔH_f^c [KJ mol^{-1}]	D^d [m s^{-1}]	P^e [GPa]	IS^f [J]	FS^g [N]	OB^h [%]
3	—	1.799^i	—	—	—	—	—	—
4	178	1.864^i	−198.6	7125	21.192	>40	160	−3.5
5	161	1.674	−71.9	8002	25.155	>40	240	−19.5
6	146	1.696	−25.8	8239	28.419	>40	160	−10.9
7	166	1.670^i	81.2	8245	26.643	>40	144	−21.8
8	108	1.677	163.3	7845	23.327	>40	324	−29.4
9	137	1.668	4.0	8084	24.788	>40	240	−23
10	147	1.653	1.9	7920	23.071	>40	160	−30.5
11	185	1.680	−98.8	7861	22.917	>40	144	−29.1
TNT^j	295	1.650	−67	6881	19.5	15	—	−25

[a] Decomposition temperature (onset, DSC, 10 °C min^{-1}). [b] Density (calculated using Gaussian09). [c] Heat of formation (calculated using Gaussian09). [d] Detonation velocity (calculated with Explo5 v6.01). [e] Detonation pressure (calculated with Explo5 v6.01). [f] Impact sensitivity (BAM method). [g] Friction sensitivity (BAM method). [h] Oxygen balance (based on CO) for $C_aH_bO_cN_d$, $1600(c - a - b/2)/M_W$ (M_W = molecular weight). [i] Crystal density. [j] Ref. 20.

Hydrazinium **7** crystallizes in the monoclinic space group *P*21/*c* with four molecules per unit cell with a density of 1.670 g cm^{-3} (CCDC 2018495†). The dihedral angle between the plane of N(4)–N(5)–C(4) and oxadiazole is 88.27° (Fig. 1e). As shown in Fig. 1f, owing to the hydrogen atoms of the methyl and hydrazinium groups, lots of intermolecular hydrogen bonds are observed. The two strongest intermolecular hydrogen bonds are O(3)–H(7B) and O(2)–H(7A) with lengths of 2.10 Å and 2.21 Å and angles of 151.18° and 144.03°, respectively. The other hydrogen bonds are relatively weak with lengths of 2.63 Å to 2.99 Å and angles of 120° to 170°.

The physical properties and thermodynamic behaviour of **4–11** are shown in Table 1. Thermal stability was measured using differential scanning calorimetry (DSC) at a rate of 10 °C min^{-1}. The materials decomposed from 108 to 178 °C without melting, which proves that the cations can regulate the thermal stability of the energetic salts.

The mechanical sensitivity, comprising impact and friction sensitivity, was examined using the standard BAM method. The impact sensitivities of **4–11** are all over 40 J despite the presence of the gem-dinitro group. To the best of our knowledge, there are almost no cases of energetic potassium salts with an impact sensitivity of over 40 J.[21] According to its crystal structure, **4** is a relatively firm 3D MOF owing to the stronger interaction of K–O and the hydrogen bonds. Moreover, methylene internal rotation can also absorb impact force.

The densities and the heats of formation (HOF) of **4–11** were calculated by using Gaussian09[22] (see the ESI†) and then the detonation velocity and pressure were predicted using EXPLO5 v6.01.[23] For **4** and **7**, we used their crystal densities directly. As a result of the cross structure of (5-methyl-1,2,4-oxadiazol-3-yl) dinitromethanide, the calculated densities for this series of compounds range from 1.650 to 1.700 g cm^{-3}, while the detonation velocities and pressures of **4–11** are higher than those of TNT.

Conclusions

We have developed a new series of energetic salts based on 1,2,4-oxadiazole with a gem-dinitro group. All compounds were fully characterized by IR, ^{1}H and ^{13}C NMR, and HRMS, as well as single-crystal X-ray diffraction for **3**, **4** and **7**. At the same time, DSC and sensitivity tests towards impact and friction were carried out. The single crystal of **3** was used to confirm the structure of the intermediate for the first time while the single crystal of **4** gave the structure of the 3D MOF. Moreover, the energetic salts show satisfactory impact sensitivity, good explosive performance and acceptable friction sensitivity. Compound **7** decomposes at 166 °C with a detonation pressure of 26.6 GPa and a detonation velocity of 8245 m s^{-1}, which could be a potential practical energetic material like TNT. In combination with 5-methyl-1,2,4-oxadiazol, gem-dinitro-derived energetic salts demonstrate amazing low sensitivity with the thermal stability regulated by different cations, which gives new insight into gem-dinitro-derived compounds.

Conflicts of interest

There are no conflicts to declare.

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