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COMMUNICATION

Synthesis and Characteristics of Novel, High-Nitrogen 1,2,4-Oxadiazoles

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Two novel high-nitrogen energetic compounds 3-azido-5-guanidino-1,2,4-oxadiazole (AOG, N% 66.65) and 3,6-bis(3'-azido-1',2',4'-oxadiazole-5'-guanyl)-1,2,4,5-tetrazine (AOG₂Tz, N% 67.62) were synthesized and fully characterized. The thermal stability of them was evaluated with differential scanning calorimeter (DSC). AOG and AOG₂Tz decomposed at 196 °C and 210 °C, respectively. They exhibit high density, favourable detonation properties, and they are low sensitive to impact.

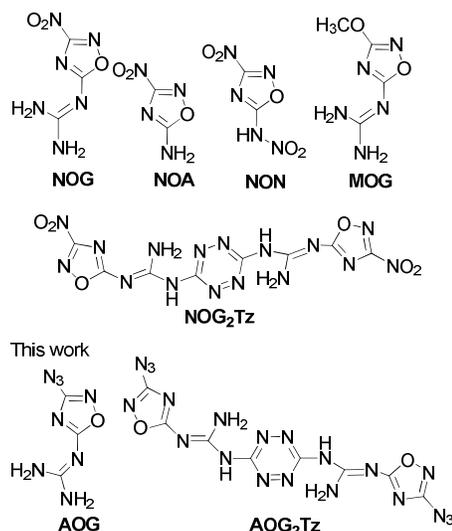
As one class of useful and promising structures for the design and synthesis of high-energy density materials (HEDMs), high-nitrogen, heterocyclic compounds usually offer high enthalpy of formation and good thermal stability.¹ Molecules with high nitrogen, while low hydrogen and carbon content can achieve a good oxygen balance easily, therefore, they were extensively used as high explosives and ingredients of propellants.² There are generally two common methods to increase the nitrogen content of compounds. One is the introduction of 1,2,4,5-tetrazine ring, (N%, 68.3), a famous high nitrogen energetic heterocyclic group, which is a very effective structural unit for designing insensitive high energetic materials.³ Energetic materials based on tetrazine always show the desirable properties of high nitrogen content, excellent kinetic and thermal stabilities due to tetrazine's aromaticity.⁴ Another method is to employ azido moiety,⁵ which will increase the heat of formation and nitrogen content of the resulting compounds sharply, and will further highlight the high-nitrogen advantages and provide greater application prospect.

With these features in mind, our research group became interested in examining the compounds containing both the tetrazine and azido group. It is expected that the combination of 1,2,4-oxadiazole fragment with energetic tetrazine backbone and azido group will give rise to new compounds with better properties. We have prepared a series of compounds containing 1,2,4-oxadiazole ring (Figure 1). 1,2,4-Oxadiazole is an isomer of furazan⁶ with a more positive calculated enthalpy of formation.⁷ Our previous results showed that the introduction of the 1,2,4-oxadiazole ring to explosives increases the thermal stability and simultaneously decreases the sensitivity. Herein, 1,2,4-oxadiazole-based novel high nitrogen explosives are reported.

As a continuous study of 1,2,4-oxadiazole-based energetic materials, we herein report the synthesis and characterization of 3-azido-5-guanidino-1,2,4-oxadiazole (AOG, N% 66.65) and 3,6-bis(3'-azido-1',2',4'-oxadiazole-5'-guanyl)-1,2,4,5-tetrazine

(AOG₂Tz, N%, 67.62). AOG and AOG₂Tz may be a new class of energetic materials bearing azido group which have good thermal stability, high densities, high nitrogen and high heats of formation. Especially AOG₂Tz contains 1,2,4-oxadiazole, azido and tetrazine moieties in one molecule.

Previous work



This work

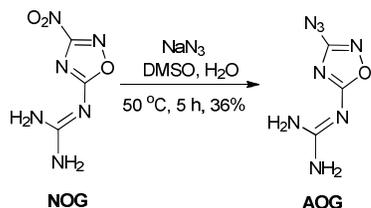
Fig.1 Some 1,2,4-oxadiazole-based explosives.

3-Methoxy-5-guanidino-1,2,4-oxadiazole (MOG) was obtained in the research during exploring the preparation of 3,6-bis(3'-nitro-1',2',4'-oxadiazole-5'-guanyl)-1,2,4,5-tetrazine (NOG₂Tz) in our precious work (Figure 1).^{7b}

The thermal stability of MOG was evaluated with differential scanning calorimeter (DSC). The test results of NOG and MOG were compared to find that the thermal stability of NOG (T_{dec} 290 °C)^{7a} is much higher than those of MOG (T_{dec} 260 °C)^{7b}. It is the result of hydrogen bonding opportunity between nitro and the guanidine groups that enhances stability and density.

After MOG was obtained successfully, the azido group was considered to be introduced into the 1,2,4-oxadiazole ring by nucleophilic substitution reaction, hoping to improve the detonation performance through increasing the nitrogen content and formation enthalpy. Thus, the target product AOG (N% 66.65) was yielded easily by the reaction of NOG with NaN₃ in DMSO/H₂O at 50 °C, 36% yield (Scheme 1). The reaction mixture was simply quenched with ice water giving the

precipitation of pure products was obtained. And AOG was fully characterized with IR, ^1H NMR, ^{13}C NMR as well as elemental analysis.⁸ AOG decomposed at 196 °C measured by DSC, indicating that it shows lower thermal stability than NOG.

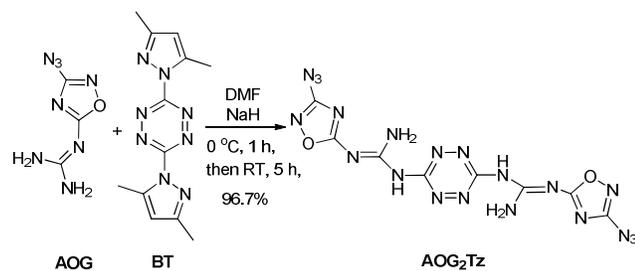


Scheme 1 Synthesis of AOG.

Aiming at further enhancing the detonation performance of AOG and increasing the nitrogen content and thermal stability, it would be valuable to introduce the tetrazine ring into AOG.

AOG₂Tz was prepared by the reaction of AOG and 3,6-bis(3',5'-dimethylpyrazol-1'-yl)-1,2,4,5-tetrazine (BT) in an excellent yield (96.7%, Scheme 2). The structure of AOG₂Tz was confirmed by IR, ^1H NMR, ^{13}C NMR as well as HRMS.⁸ The nitrogen content of AOG₂Tz (N%, 67.62) was higher than that of AOG. AOG₂Tz decomposed at 210 °C, indicating that it was more thermal stable than that of AOG (T_{dec} 196 °C). We can conclude from this result that the introduction of the tetrazine ring to the explosive molecule can increase the thermal stability. And AOG₂Tz possesses higher thermal stability than 3,6-bis(3'-azido-1',2',4'-triazol-1'-yl)-1,2,4,5-tetrazine (BATTz) (T_{dec} 172 °C),^{5b} which shows that introduction of 1,2,4-oxadiazole ring improves the thermal stability.

Although no nitro group in the molecular structure of AOG₂Tz intramolecular hydrogen bond interactions make it a plane geometry (Figure 3). This property enhances density and stability by giving a more planar structure. These two symmetric amino groups in the molecule are fixed in the molecular plane and can't rotate freely. Therefore, $-\text{NH}_2$ protons in AOG₂Tz are located in different chemical environment. It is likely that the NH_2 are hydrogen bonded to the adjacent tetrazine ring nitrogen atoms as seen for NOG₂Tz. The ^1H NMR spectra of AOG₂Tz and NOG₂Tz are thus similar. The protons of $-\text{NH}_2$ in AOG₂Tz have different chemical shifts at 9.05 and 8.80 ppm.^{7b}



Scheme 2 Synthesis of AOG₂Tz.

The structure of AOG and AOG₂Tz were optimized to obtain their molecular geometries by using the density quantum chemistry functional method DFT-B3LYP/6-31G* level. The results show that the molecules of AOG and AOG₂Tz are almost coplanar (Figures 2, 3). The molecular configuration of AOG₂Tz

is in good agreement with ^1H NMR spectra. The calculated crystal maximum predictive densities of AOG and AOG₂Tz were 1.694 g cm⁻³ and 1.734 g cm⁻³, respectively.

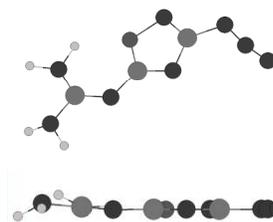


Fig. 2 The optimized molecular geometry of AOG.

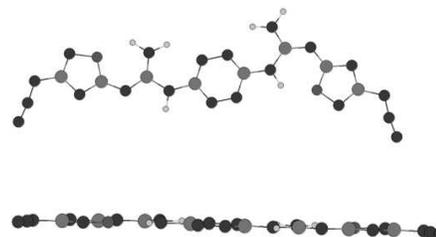


Fig. 3 The optimized molecular geometry of AOG₂Tz.

To investigate the energetic properties of AOG and AOG₂Tz, experiments and calculations are carried out with results listed in Table 1. Drop hammer tests gave the impact sensitivities of them as 20 J and 30 J, which shows these two azido compounds are good explosives with low impact sensitivity. Their detonation performances were calculated based on the single crystal density and theoretical heat of formation with MOPAC/PM6. The theoretical heat of formation of AOG and AOG₂Tz is 535 kJ mol⁻¹, 1564 kJ mol⁻¹, respectively, which is the extremely positive heat of formation.⁹ Using the calculated values for the density and the heat of formation, the detonation velocity and the detonation pressure of AOG and AOG₂Tz were predicted to be 7630 m s⁻¹ and 24.89 GPa, 7592 m s⁻¹ and 25.0 GPa, respectively (Table 1).

Conclusions

In summary, new high-nitrogen energetic compounds, AOG (N% 66.65) and AOG₂Tz (N% 67.62) were prepared by nucleophilic substitution reaction of NOG with NaN_3 and condensation of AOG with BT, respectively. In the case of azido, the thermal stability is significantly low. Anyway, in the presence of 1,2,4-oxadiazole ring, the thermal decomposition temperatures of AOG and AOG₂Tz are still high, close to 200 °C. It further verifies that the introduction of 1,2,4-oxadiazole ring into explosives can improve the thermal stability.⁷ Further research should be focused on insensitive explosives containing 1,2,4-oxadiazole ring.

Caution! When handling these energetic materials, personal safety precautions must be always applied.

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Table 1 Physico-chemical properties and detonation performances of AOG, and AOG₂Tz.

Compd.	$T_{\text{dec.}}^a/$ °C	Density ^{b/} g cm ⁻³	$\Delta H_f^{\theta c/}$ kJ mol ⁻¹	$IS^d/$ J	$P^e/$ GPa	$D^f/$ m s ⁻¹
AOG	196	1.694 ^g	535	20	24.89	7630
AOG ₂ Tz	210	1.734 ^g	1564	30	25.0	7592
NOG ^h	290	1.766	235	>40	28.16	8013
NOG ₂ Tz ⁱ	328	1.812 ^g	957	>70	28.52	8002
TNT ^j	295	1.65	-67.0	15	19.53	6881
RDX ^k	230	1.82	92.6	7.4	35.17	8997

^a Thermal degradation (DSC, 10 °C min⁻¹). ^b Single crystal density. ^c Heat of formation (MOPAC PW6). ^d Impact sensitivity (BAM drop hammer). ^e Detonation pressure. ^f Calculated detonation velocity. ^g Calculated (B3LYP/6-31G*). ^h Ref[7a]. ⁱ Ref[7b]. ^j Ref[9].

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Notes and references

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¹⁵ † Electronic Supplementary Information (ESI) available: Experimental details, differential scanning calorimeter (DSC) figures for AOG, AOG₂Tz. For ESI, See DOI:10.1039/b000000x/

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Two novel high-nitrogen energetic compounds AOG and AOG₂Tz were prepared with good performance, high thermal stability and low impact sensitivity.

