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## Introduction

Design and synthesis of simple structures with excellent performances have always been an unswerving pursuit for the development of energetic materials.<sup>1-4</sup> Over the past decades, the aliphatic nitramine (-NNO<sub>2</sub>) based structures have proved to be the most powerful energetic materials available and they have largely superseded the aromatic -CNO<sub>2</sub> structures such as TNT for military applications.<sup>5-7</sup> Due to the advantages of low cost, easy access and structural diversity, monocyclic nitramines have attracted intense attention, among them, monocyclic nitramines based on 1,3,5-triazacyclohexane and 1,3,5,7tetraazacyclooctane backbones (RDX and HMX) are still the most important practical explosives with high brisance and satisfactory stability. From a synthetic perspective, diversityoriented synthesis of high energetic monocyclic nitramines with pyrimidine backbones is more achievable than those with other backbones such as 1,3,5-triazacyclohexane or 1,3,5,7tetraazacyclooctane. While retaining the nitramine (-NNO<sub>2</sub>)

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# Synthesis and properties of azamonocyclic energetic materials with geminal explosophores<sup>†</sup>

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Diversity-oriented synthesis of energetic pyrimidine structures with geminal explosophoric groups of geminal dinitro and azido-nitro groups *via* a novel reductive cleavage and oxidative coupling strategy is reported. Fluorine has also been introduced for the first time based on the nucleophilic coupling process. The obtained energetic pyrimidines are investigated *via* X-ray diffraction and theoretical techniques of electrostatic potential and proton affinity calculations. Both experimental and calculation results showed impressive detonation performances and good application prospects of the energetic pyrimidine structures. Among them, DNNC exhibited great promise as a green oxidant in solid propellant formulations to replace ammonium perchlorate (AP). TNHA ( $\rho = 1.79$  g cm<sup>-3</sup>, D = 8537 m s<sup>-1</sup>, P = 32.69 Gpa) and TNHF ( $\rho = 1.85$  g cm<sup>-3</sup>, D = 8517 m s<sup>-1</sup>, P = 32.64 Gpa) proved to be ideal candidates for high explosives due to their high densities and detonation properties. Moreover, TNHA could also be applied as a potential underwater explosive owing to its great heat of formation.

moieties, additional geminal explosophoric groups can be constructed in the C-3 center of the pyrimidine backbones, giving combined energetic structures with both nitramine (–NNO<sub>2</sub>) and C-3 based geminal explosophoric groups.<sup>8,9</sup>

Our recent studies on energetic 1,3-oxazinane structures have proved that the introduction of geminal dinitro and azido-nitro explosophoric groups will lead to distinct physiochemical and energetic properties. Despite the attractive application prospects of geminal explosophoric groups, currently applied methods to synthesize them suffer from complicated post-treatment procedures, which often lead to complex mixtures of products.<sup>10-14</sup> Herein, we report a novel selective reductive cleavage and oxidative coupling strategy for the diversity-oriented synthesis of energetic pyrimidine structures with geminal explosophoric groups such as geminal dinitro and azido-nitro groups.<sup>10,15</sup> The novel reductive cleavage reaction exhibited great chemical selectivity, and the presence of nitramine groups played key roles in the successful C-Br cleavage. Based on the cleavage product 1,3,5-trinitrohexahydropyrimidine, another coupling strategy through nucleophilic substitution was also proved achievable, with fluorine successfully introduced into the energetic pyrimidines for the first time. Comprehensive structural and performance studies on the obtained energetic materials were performed using both experimental and calculation methods, with the effects of different geminal explosophoric groups on the corresponding properties of the new energetic pyrimidines being analyzed and compared systematically (Fig. 1).



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## **Results and discussion**

#### Synthetic studies of energetic pyrimidine structures

Investigations commenced by developing a method for constructing the pyrimidine backbone, based on which explosophoric groups could be incorporated through the reductive cleavage and oxidative coupling strategy we designed. The desired structure of 5-bromo-1,3-di(tert-butyl)-5-nitro-hexahydropyrimidine (DBBrP) was assembled through an efficient one-pot Mannich condensation reaction between 2-bromo-2nitro-1,3-propanediol, formaldehyde and tert-butylamine. The blocking tert-butyl groups were essential to avoid multiple condensations, and could be removed readily under treatment with 98% HNO<sub>3</sub>, leading to the nitrolysis product 1,3,5-trinitro-5-bromo-1,3-diazacyclohexane (TNBrP). TNBrP was set for the pivotal C-Br cleavage reaction,<sup>16,17</sup> which we approached with some trepidation since it would require overcoming the high steric hindrance at the quaternary carbon center. Studies on the C-Br cleavage reaction were first carried out with the addition of some strong hydride donors, such as NaH, LiAlH<sub>4</sub>, DIBAL-H and AlH<sub>3</sub>.<sup>18-21</sup> Unfortunately, the cleavage reaction proved to be extremely challenging as none of the methods gave the desired product. After some unsuccessful trials and detours, we finally found that NaBH<sub>4</sub> reduction could successfully cleave the C-Br bond selectively, affording the desired structure of 1,3,5-trinitrohexahydropyrimidine (TNHP) in a

yield of 78%. Interestingly, the existence of nitramine  $(-NNO_2)$  moieties proved to be crucial for this transformation since similar hydride donors, including the NaBH<sub>4</sub> system, were not able to cleave the C–Br bond in DBBrP (Scheme 1).

For a better understanding of the selective reduction strategy in energetic structures, we carried out a computational experiment to investigate the effect of nitramine (-NNO<sub>2</sub>) on the outcome of the C-Br cleavage process<sup>22,23</sup> (Scheme 2). Due to the stereoelectronic effect, there were two stable configurations of TNBrP, I1a and I1b, in which the energetic -NNO<sub>2</sub> moieties were in axial bond positions. The -NNO2 then coordinated with solvated NaBH<sub>4</sub> giving the complex molecules I2a and I2b. A nucleophilic substitution would trigger the C-Br bond cleavage, and there were four possible transition states of the substitution reaction as shown in TS3a, TS3b, TS3c and TS3d. Among them, TS3a was the most stable one with a reaction energy barrier of 32.8 kcal  $mol^{-1}$ . Under the guidance of the -NO<sub>2</sub>, a hydride was transferred from the -BH<sub>4</sub> to the quaternary carbon and the C-Br bond was cleaved. Finally, Br<sup>-</sup> combined with BH<sub>3</sub> would remove the solvated NaBH<sub>3</sub>Br and the target compound TNHP was obtained with the total reaction energy of -43.6 kcal mol<sup>-1</sup>.

After the cleavage of the C–Br bond, our focus then shifted to the diversity-oriented synthesis of geminal explosophoric groups *via* an oxidative coupling strategy. Exposure of TNHP to sodium hydroxide and potassium ferricyanide promoted the



Scheme 1 Reaction route of carbon-bromine cleavage reduction.



Scheme 2 Calculated reaction mechanism of C-Br cleavage reduction of NaBH<sub>4</sub>.

oxidative coupling with NaN<sub>3</sub> or NaNO<sub>2</sub>. The desired new explosophoric groups of geminal dinitro and azido-nitro groups were achieved, giving the energetic pyrimidines of DNNC and TNHA in good yields (78.4% and 19.6%). Moreover, the secondary cyclic nitroalkane salts of TNHP were also perfect and stable nucleophiles for similar couplings through nucleophilic substitutions. For instance, a novel fluorinated energetic pyrimidine was successfully achieved in such ener-

getic systems for the first time through this nucleophilic substitution of TNHP's potassium salt with Selectfluor®, a rationally designed reagent that successfully provides an "F +" equivalent as the electrophile<sup>24</sup> (Scheme 3).

#### Single-crystal X-ray diffraction

Single crystals of the high energetic molecules of DNNC and TNHA, which were suitable for X-ray crystal-structure determi-



nation, were obtained from aqueous solution. Both of them exhibited high crystal densities of 1.815 g cm<sup>-3</sup> (DNNC) and 1.789 g cm<sup>-3</sup> (TNHA). As shown in Fig. 2(a) and (b), in contrast to the highly close molecular formulas of the two pyrimidine structures, there is a clear distinction between their molecular structures. The different explosophoric groups have a huge influence on their crystal structures. DNNC crystallized in the orthorhombic space group  $P2_12_12_1$  with twenty-four molecules per unit cell; in contrast, TNHA crystallized in the monoclinic space group Cc (TNHA) with four molecules per unit cell (Fig. 2c and d). The selected crystallographic data of DNNC and TNHA, measurement parameters and refinement details are listed in the ESI.<sup>†</sup>

Based on the crystal structure analysis, the compounds of TNHA and TNHP all belong to the monoclinic space group with presenting chair conformations, while DNNC belongs to the orthorhombic space group. The special space group and crystal system of DNNC extend it into the space in two directions as shown in Fig. 2(c), and the weak interaction forces, N-N and N-O, connect the individual molecules. Compared with the spatial structures of TNHP and TNHA in Fig. 2(d), the -NO<sub>2</sub> in DNNC piles up closer for its planar and conjugated structure, which benefit in reducing energy and maintaining stability. The average bond lengths of the C-N bonds of DNNC and TNHA are both about 1.45 Å, which is shorter than that of the typical C-N single bond (1.48 Å). And the C-C average bond length in the skeleton is also 0.02 Å shorter than that of the normal one. Meanwhile, the bond angles of the atom in the ring ranging from 109.05°-111.89° are very close to the

angle of the sp<sub>3</sub> hybrid orbital, 109.5°. It is the shorter bond length and the close bond angle that make the ring skeleton relatively stable and further reduce the sensitivity. However, it is puzzling that the nitrate amino groups (N-NO<sub>2</sub>) in the hexahydropyrimidine ring are all in the position of axial bonds instead of equatorial ones, where the theoretical energy is the lowest. The mutual action between multiple groups with high steric resistance affects each other causing the notro groups to be in axial bonds.

#### Hirshfeld and electrostatic potential analysis

Hirshfeld surfaces have been widely applied to identify and quantify the interaction nature and proportion in crystals. Herein, Hirshfeld surfaces of DNNC and TNHA molecules associated with two-dimensional fingerprint spectra were employed to investigate their intermolecular interactions, with the results presented in Fig. 3. For energetic materials, it has been proved that the O····H and N···H interactions contribute to decrease the mechanical sensitivities by absorbing the external stimuli whereas the O…O interactions always lead to a less stable structure and higher sensitivities. For Hirshfeld surface analysis, the red and blue areas on the surfaces denote the high and low close contact populations, respectively. The calculated results showed that the O…H contact interactions of DNNC account for 28.4%, which was much higher than that of TNHA. This is a high coincidence with the sensitivity data from the experiments, which showed that the impact sensitivity of DNNC and TNHA were 22 J and 7 J, respectively.

The surface electrostatic potential (ESP) is regarded as an effective tool for interpreting and predicting the reactive behaviors of molecules with high proton affinity.<sup>38-40</sup> To clarify the distribution of electrons in the highly similar energetic pyrimidine molecules and explain the distinctions of sensitivity between them, ESP studies of DNNC, TNHA and TNHF were calculated based on the Gaussian software at the B3LYP/ 6-31+g(d,p) level with the optimized structures. In addition, we also calculated the ESPs of TNHP and DNHM to obtain more convincing comparative results. It has been generally accepted that the extent and density of electropositive potential surfaces are positively associated with impact sensitivity. In Fig. 4, it was clear that the positive ESP region and charge separation of TNHP and DNHM were almost the same for each, indicating very close impact sensitivities, which were in good agreement with the experimental data ( $H_{50}$  (5 kg) of TNHP and DNHM: 45 cm and 47 cm, respectively). In contrast, due to the smaller ESP region and lower charge separation, DNNC would show better impact sensitivity than TNHA and TNHF, which could further explain the experimental results.

#### Thermal behavior

Thermal stability is one of our primary concerns since it is a particularly crucial property of any energetic material in practical use; therefore, the thermal behaviors of both DNNC and TNHA were investigated and compared. Although sharing the same pyrimidine backbones, the thermal behaviors of DNNC and TNHA showed a huge difference. The decomposition temperatures of DNNC and TNHA were 209.6 and 151.3 °C,





decomposition processes of both DNNC and TNHA were observed at 125.9 and 149.1 °C, from the DSC experiments, indicating the existence of melting processes. Obviously, the difference in thermal stabilities between DNNC and TNHA was caused by the  $-NO_2$  and  $-N_3$  moieties. Like most azido based energetic structures, the lower stability of TNHA was most possibly caused by the high activity of the azido group. Also, when it explodes or burns, TNHA with azido will produce more soot compared with DNNC. Meanwhile, the TG curve revealed that DNNC was decomposed more completely than that of

respectively (Fig. 5). Small endothermic peaks for the

TNHA, which indicated that DNNC broke down more thoroughly during the heating process.

To investigate the non-isothermal kinetics of thermal decompositions of DNNC and TNHA, DSC curves at different heating rates were employed at four different heating rates of 5, 10, 15, and 20 K min<sup>-1</sup> (Fig. 5 and 6). All the melting and decomposition temperatures increased with the increase of the heating rates. Both Kissinger and Ozawa<sup>25,26</sup> methods were employed to calculate the kinetic parameters (apparent activation energy ( $E_a$ ) and pre-exponential constant (A)) of the decomposition reaction of DNNC and TNHA.



(b)

(a)

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Fig. 3 Hirshfeld surfaces, 2D fingerprint plots and the individual atomic contact percentage contribution of (a) DNNC and (b) TNHA.



Fig. 4 Calculated ESPs of the energetic compounds (a) TNHP, (b) DNHM, (c) DNNC, (d) TNHA and (e) TNHF.

The Kissinger and Ozawa methods are expressed in eqn (1) and (2):

$$\ln \frac{\beta_{\rm i}}{T_{\rm pi^2}} = \ln \frac{AR}{E_{\rm k}} - \frac{E_{\rm k}}{RT_{\rm pi}}, \eqno(1)$$

$$\log \,\beta_{\rm i} + \frac{0.4567 E_0}{R T_{\rm pi}} = C, \eqno(2)$$

where  $T_p$  is the peak temperature (K);  $E_a$  is the apparent activation energy (kJ mol<sup>-1</sup>);  $\beta$  is the linear heating rate; R is the gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>); and A is the pre-exponential factor (s<sup>-1</sup>).

The apparent activation energy  $E_k$  of TNHA obtained from Kissinger's method<sup>25</sup> at atmospheric pressure was 797.4 kJ mol<sup>-1</sup>, which was in good agreement with  $E_0$  obtained from Ozawa's method<sup>26</sup> (786.6 kJ mol<sup>-1</sup>). Moreover, the calculated apparent activation energy value of TNHA was only half of the calculated result of DNNC, which meant the thermal stability of DNNC would be much better than that of TNHA. The calculation results were consistent with the results based on DSC-TG experiments.

#### Physiochemical and energetic properties

The heat of formation  $(\Delta_t H)$  of energetic pyrimidines, including DNNC, TNHA and TNHF, were calculated using Gaussian



Fig. 5 DSC traces of DNNC and TNHA.



 $09^{27}$  with the program at the B3LYP/6-31+g (d,p)<sup>28,29</sup> level of theory. The optimal structures were characterized to be true local energy minima on the potential-energy surface without

imaginary frequencies. Then the enthalpy of formation was obtained from the gas phase heat of formation, which was calculated by the atomization method using Gaussian 09<sup>27</sup> with Trouton's rules.<sup>30</sup> On the basis of the densities of crystal and enthalpy of formation, the general detonation properties of the obtained energetic pyrimidines and of some similar energetic structures were estimated by EXPLO5<sup>31,32</sup> and are listed in Table 1.

Compared to C-3 multiple substituted compounds DNNC, TNHA and TNHF, the compounds TNHP and DNHM showed a lower energy level. However, the low melting points and great sensitivities of TNHP and DNHM make them potential candidates for the development of melt-casting explosives. The high nitrogen content and enthalpy of formation of TNHA and TNHF will make it possible for them to be ideal candidates for high explosives. The balanced and outstanding performance of DNNC shows great prospects in the propellant field.

#### Propulsion properties

The high oxygen content and high enthalpy of ammonium perchlorate  $(AP)^{36}$  make it the most important high-energy oxidant that is extensively used in composite solid propellants. However, there are some severe defects of AP during its applications, such as low heat of formation (-295.8 kJ mol<sup>-1</sup>), low specific impulse (157 s, value calculated using EXPLO5/6.02), high detectable smoke signal and the generation of hydrogen chloride during burning caused by the chlorine content.

Compounds	$ ho/ m g~cm^{-3}$	$T_{\rm c}{}^a/K$	$\Omega/\%$	$M_{ m w}^{\ \ b}$	C* <sup>c</sup> / m s <sup>-1</sup>	$I_{\rm SP}{}^d/$ N S kg <sup>-1</sup>
DNNC	1.82	3453.6	-18.0	25.7	1654.9	2661.9
TNHA	1.79	3218.6	-30.5	23.6	1634.6	2567.7
TNHF	1.85	2897.5	-30.1	23.883	1534.2	2406.1
RDX	1.80	3277.3	-21.6	24.3	1644	2608.9
AP	1.95	1434.2	4.0	27.9	990.0	1556.0

<sup>*a*</sup> Chamber temperature. <sup>*b*</sup> Relative average molecular mass of the products. <sup>*c*</sup> Characteristic velocity. <sup>*d*</sup> Specific impulse.

Table 1	Physical and energet	tic properties of TNHP	, DNNC, TNHA and TNH	F compared with the com	pounds DNHM and RDX
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Compound	TNHP	DNHM <sup>j 33</sup>	DNNC	TNHA	TNHF	RDX <sup>34,35</sup>
Formula	C <sub>4</sub> H <sub>7</sub> N <sub>5</sub> O <sub>6</sub>	C <sub>4</sub> H <sub>7</sub> N <sub>5</sub> O <sub>7</sub>	C <sub>4</sub> H <sub>6</sub> N <sub>6</sub> O <sub>8</sub>	C <sub>4</sub> H <sub>6</sub> N <sub>8</sub> O <sub>6</sub>	C <sub>4</sub> H <sub>6</sub> N <sub>5</sub> O <sub>6</sub> F	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>
Molar mass	221.1	237.0	266.0	262.0	239	222.1
$N + O^{a} / \%$	31.8	29.5	31.6	42.7	29.29	81.0
$\rho^{b}/\mathrm{g}\mathrm{cm}^{-3}$	1.79	1.76	1.82	1.79	1.85	1.80
$\Omega^{c}/\%$	-39.8	-30.4	-18.0	-30.5	-30.13	-21.6
$\Delta H_{\rm f}^{\ d}/{\rm kJ}~{\rm mol}^{-1}$	-50.49	128.62	46.05	308.74	-242.82	86.3
$v_{\rm D}^{e}/{\rm m~s^{-1}}$	8388	8412	8763	8686	8517	8823
P <sup>f</sup> /Gpa	29.88	31.59	34.97	32.69	32.64	35.1
$I_{\rm S}^{g}/J$	22.5	23.5	21.9	7.0	_	7.4
$T_{\rm mel}^{h/o}C$	_	126.9	154.7	121.1	_	205.5
$T_{\rm dec}^{i/\circ} C$	150.6	197.0	222.2	143.2	—	210

<sup>*a*</sup> Nitrogen and oxygen contents. <sup>*b*</sup> Crystal density except TNHF (calculated density). <sup>*c*</sup> Oxygen balance. <sup>*d*</sup> Calculated heat of formation. <sup>*e*</sup> Detonation velocity. <sup>*f*</sup> Detonation pressure. <sup>*g*</sup> Impact sensitivity. <sup>*h*</sup> Melting points. <sup>*i*</sup> Decomposition points. <sup>*j*</sup> 1,3-Dinitrohexahydropyrimidin-5-yl nitrate.



Fig. 7 DSC traces of TNA at various heating rates.

Therefore, intensive effort has been devoted to synthesize new materials to cooperate with AP, providing more oxygen and energy in propellant formulations currently. RDX is the most widely applied organic oxidant in composite solid propellants. To investigate the application prospects of DNNC, TNHA and TNHF in propellants, the parameters of propulsion performance, including theoretical specific impulse ( $I_{sp}$ ), characteristic

 Table 3
 Effect of DNNC content on the energy characteristics of the CMDB propellant

Compound ratio RDX : DNNC	$T_{\rm c}/{ m K}$	$M_{ m w}$	$C^*/m \ s^{-1}$	$I_{\rm SP}/{ m N~S~kg^{-1}}$	$\Omega/\%$
31:0	3265.9	26.31	1590.1	2553.3	-15.1
26:5	3274.7	26.39	1590.5	2556.0	-14.9
21:10	3283.2	26.47	1590.7	2558.6	-14.7
16:15	3291.5	26.56	1590.9	2561.1	-14.5
11:20	3299.5	26.64	1591.0	2563.5	-14.4
6:25	3307.4	26.72	1591.1	2665.9	-14.2
0:31	3316.6	26.82	1591.0	2568.6	-13.9

velocity ( $C^*$ ) and fuel temperature ( $T_c$ ), were confirmed *via* NASA-CEA<sup>41</sup> in the standard state (pressure is 6.86 MPa and expansion ratio is 70:1) (Table 2).

Compared with AP, RDX, TNHA and TNHF, DNNC exhibited high energy level and specific impulse, as well as nice oxygen balance, which make it possible to be a new high-energy propulsive solid filler with low pollution and signal. In particular, DNNC has outstanding advantages. The laser ignition tests were then carried out to further investigate the propulsion applications and combustion mechanism of DNNC (Fig. 8). We chose DNNC and RDX as separate samples to be excited by a laser under different power densities. The ignition delay time was recorded to reflect the sensitivity of various materials to laser energy with the diagram of the test device and results listed in Fig. 7. Fig. 7 shows that the ignition delay time of both DNNC and RDX was closely related to the density of power, and showed a decreasing trend with the increase of heat fluxes. As the laser power density continued to grow, the entire delay time went toward stabilization. Due to the gemdinitro structure, DNNC exhibited a faster response to the energy of the laser at low heat fluxes, which played an important role in improving ignition sensitivity.

Finally, DNNC was applied to replace RDX gradually to investigate the impact on the energy characteristics of the micro-smoke modified double base propellant (Table 3). The original propellant formula was nitrocellulose (NC) of 25%, nitroglycerin (NG) of 33%, RDX of 31%, DINA of 3.5% and some other additives of 7.5%. The calculation results showed that the applications of DNNC may bring a bright prospect in the field of micro-smoke modified double base propellants. Compared to RDX based propellants, the addition of DNNC increased the chamber temperature, indicating greater heat released during the burning, which would be very helpful to promote  $I_{sp}$ . This was further proved by the calculated results of  $I_{\rm sp}$ . Moreover, the oxygen balance of the mixed components was also well improved. All these results showed that DNNC could be an ideal candidate to replace RDX in propellants as a new high-energy oxygen-supplying material.



Fig. 8 Ignition delay time of DNNC and RDX at different power densities (a) and schematic of the customized laser ignition test setup (b).

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Unlike DNNC, the energetic pyrimidines of TNHA and TNHF exhibited different application prospects. Due to the high nitrogen content and low melting point, TNHA showed superior sensitivity and detonation performance than nitroglycerin (NG),<sup>37</sup> which makes it an ideal candidate material for an energetic plasticizer. TNHA could also be applied as a potential underwater explosive owing to its great heat of formation. Meanwhile, the introduction of fluoride into the energetic pyrimidine backbone led to an impressive density level and detonation properties. Therefore, TNHF exhibited a great promise for potential applications as a high explosive.

## Conclusions

In conclusion, we demonstrated the diversity-oriented synthesis of promising energetic pyrimidines through a novel reductive cleavage and oxidative/substitution coupling strategy. The detailed structures of these energetic pyrimidines were characterized and the single crystal analysis of DNNC and TNHA proved that the different explosophoric groups have a huge influence on their crystal structures. Hirshfeld surfaces of DNNC and TNHA associated with two-dimensional fingerprint spectra were investigated, which showed that the O···H contact interactions of DNNC were much higher than that of TNHA and had a high coincidence with the sensitivity data from the experiments. With the same pyrimidine backbones, the thermal behaviors of DNNC and TNHA showed a huge difference and decomposition temperatures of DNNC and TNHA were 209.6 and 151.3 °C, respectively. Physiochemical and energetic properties of DNNC, TNHA and TNHF were also determined through both experimental and calculation methods. Among the three, DNNC exhibited great promise as a green oxidant in solid propellant formulations to replace AP and RDX. TNHA ( $\rho$  = 1.79 g cm<sup>-3</sup>, D = 8537 m s<sup>-1</sup>, P = 32.69 Gpa) and TNHF ( $\rho$  = 1.85 g cm<sup>-3</sup>, D = 8517 m s<sup>-1</sup>, P = 32.64 Gpa) were proved to be ideal candidates for high explosives due to their high densities and detonation properties. Moreover, TNHA could also be applied as a potential underwater explosive owing to its great heat of formation.

## Experimental

**Caution!** Although we have experienced no explosion accident during the synthesis and characterization, adequate protection should be adopted.

#### **Reagents and materials**

All reagents and solvents were purchased from Aladdin Bio-Chem Technology Co., Ltd (Shanghai, China) and used without further purification unless otherwise indicated.

#### Apparatus and measurements

The <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra of the compounds synthesized in this work were recorded on 500 MHz nuclear magnetic resonance spectrometers (Bruker AV. 500). Infrared spectra were measured using an Equinox 55 Fourier transform infrared spectrometer (Bruker, Germany). Elemental analyses were performed using a Vario EL cube elemental analyzer (Elementar, Germany). The differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) data were obtained using a model TG-DSC STA 499 F3 instrument (NETZSCH, Germany). The experiment was carried out under a dynamic nitrogen atmosphere at a temperature between 25 and 300 °C. The heating rate was 10 °C min<sup>-1</sup> and the sample scale was 0.5-1.0 mg with the aluminum plate. The molecular weight was confirmed using a high-resolution mass spectrometer (9.4T FT-ICR MS, Bruker Solarix, Germany). The diffraction data for compounds mentioned in this paper were collected using a Bruker Apex II CCD diffractometer and the specific test parameters are shown in the ESI.† The quantum chemical calculations were carried out using the Gaussian 09 program package and visualized using GaussView 5.08. The geometric optimization and frequency analyses of the structures were carried out using the B3LYP functional with 6-31+G\*\* basis set.

#### Synthetic procedures

5-Bromo-1,3-di(tert-butyl)-5-nitro-hexahydropyrimidine (DBBrP). To a stirred solution of 2-bromo-2-nitro-propane-1,3diol (18.00 g, 0.090 mol) in methanol (100 mL) at 0 °C, tertbutyl-amine (13.50 g, 0.185 mol) was added dropwise over 45 min. The mixture was stirred at 0 °C for an additional 45 min. Then, 37% formaldehyde solution (7.46 g, 0.092 mol) was added in one portion. The resulting mixture was stirred at 50 °C for 5 h and cooled to 0 °C, and then 150 mL water was added. The slight yellow solid 5-bromo-1,3-di(tert-butyl)-5nitro-hexahydro-pyrimidine (23.20 g) was collected by filtration, recrystallized from water-ethanol and washed with water, and was obtained in a yield of 80.06%. <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>) δ: 4.55 (dd, 2H), 5.15 (dd, 2H), 5.31 (m, 1H), 5.63 (d, 1H), 6.67 (d, 1H); <sup>13</sup>C NMR (125 MHz, acetone-*d*<sub>6</sub>) δ: 47.42, 60.47, 75.31; IR (KBr, ν/cm): 2971, 1558, 1365, 1346, 1031, 948, 935, 762; Anal. Calcd for C<sub>12</sub>H<sub>24</sub>BrN<sub>3</sub>O<sub>2</sub> (%): C 44.73, H 7.51, N 13.04. Found C 44.57, H 7.448, N 12.93.

**1,3,5-Trinitro-5-bromo-1,3-diazacyclohexane (TNBrP).** 12 mL 98% concentrated nitric acid was cooled to -5 °C in an ice water bath, and DBBrP (1.00 g, 0.0031 mol) was slowly added to the solution. When the addition was completed, the reaction mixture was allowed to warm to 25 °C, stirred for 4 h, and then poured onto ice. The resulting precipitate was collected by filtration, washed with water, and dried to give a white solid 1,3,5-trinitro-5-bromo-hexahydropyrimidine (0.57 g) in a yield of 61.19%. <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>)  $\delta$ : 5.02 (d, 2H), 5.41 (d, 2H), 6.14 (d, 1H), 6.29 (d, 1H); <sup>13</sup>C NMR (125 MHz, acetone-*d*<sub>6</sub>)  $\delta$ : 56.06, 61.22, 84.03; IR (KBr,  $\nu$ /cm): 2987, 2941, 2955, 1583, 1546, 1486, 1382, 1342, 1322, 764, 753, 718; Anal. Calcd for C<sub>4</sub>H<sub>6</sub>BrN<sub>5</sub>O<sub>6</sub> (%): C 16.00, H 2.00, N 23.33. Found C 15.48, H 2.34, N 22.86.

1,3,5-Trinitrohexahydropyrimidine (TNHP). Method 1: To a solution of compound TNBrP (1.31 g, 0.0044 mol) in 30 mL

methanol, small portions of sodium borohydride (0.49 g, 0.013 mol) were added at 10 °C in 5 min. After 30 min, hydrochloric acid was added until pH = 6, and the mixture was diluted with 15 mL water. Then the precipitate was filtered off, dried, and recrystallized to give a white powder solid 1,3,5-trinitrohexahydropyrimidine (0.75 g), which was obtained in a yield of 77.72%.

Method 2: The solution of potassium iodide (0.63 g) in methanol (10 mL) at 0 °C was added to a cold solution of TNBrP (0.52 g, 0.0024 mol) dissolved in a mixed solution of methanol (8 mL) and acetic acid (8 mL). The resulting solution was stirred for 8 h at 50 °C. Water (100 mL) was added and the resulting precipitate was collected by filtration and washed with water to give a white solid 1,3,5-trinitrohexahydropyrimidine (0.20 g) in a yield of 43.09%. <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$ : 4.55 (dd, 2H), 5.15 (dd, 2H), 5.31 (m, 1H), 5.63 (d, 1H), 6.67 (d, 1H); <sup>13</sup>C NMR (125 MHz, acetone- $d_6$ )  $\delta$ : 47.42, 60.47, 75.31. IR (KBr,  $\nu$ /cm): 3082, 2956, 1569, 1526, 1389, 1357, 981, 761, 575; Anal. Calcd for C<sub>4</sub>H<sub>7</sub>N<sub>5</sub>O<sub>6</sub> (%): C 21.72, H 3.167, N 31.67. Found C 22.06, H 3.295, N 30.86. *m/z*: 220.0327.

1,3,5,5-Tetranitro-hexahydropyrimidine (DNNC). TNHP (0.5 g, 2.26 mmol) was added dropwise to a solution of NaOH (0.14 g) in water (3 mL) at ambient temperature. The mixture was cooled to 10 °C until the solution became yellow and turbid. Then, a saturated aqueous solution of sodium nitrite (0.64 g, 10.1 mmol), a saturated aqueous solution of potassium ferricyanide (0.74 g, 2.25 mmol) and sodium persulfate (0.7 g, 3.0 mmol) were added to the above solution and heated to 40 °C for 5 days. The resulting solution was extracted with ethyl acetate (25 mL  $\times$  5). After drying over magnesium sulfate, the organic phases were concentrated and evaporated to dry under reduced pressure. And then, 0.47 g pale yellow solid 1,3,5,5-tetranitro-hexahydropyrimidine was collected and recrystallized from ethanol and water in a yield of 78.4%. <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$ : 5.46 (dd, 4H), 6.31 (dd, 2H); <sup>13</sup>C NMR (125 MHz, acetone- $d_6$ )  $\delta$ : 48.94, 29.29, 107.04. IR (KBr, ν/cm): 3036, 1577, 1548, 1426, 1380, 1316, 1252, 995, 894, 805; Anal. Calcd for C<sub>4</sub>H<sub>6</sub>N<sub>6</sub>O<sub>8</sub> (%): C 18.05, H 2.27, N 31.58. Found C 18.92, H 2.68, N 32.56. m/z: 266.4941.

Azido-1,3,5-trinitrohexahydropyrimidine (TNHA). TNHP (0.5 g, 2.26 mmol) was added to 5 mL of 4% NaOH aqueous solution at room temperature and allowed to be stirred for 15 min. Then, a saturated aqueous solution of sodium azide (0.73 g, 11.2 mmol) was slowly added dropwise to the mixture and then a saturated aqueous solution of potassium ferricyanide (0.74 g, 2.25 mmol) was poured to the mixture with sodium persulfate (0.7 g, 3.0 mmol). The mixture was stirred thoroughly for 2 days with the temperature increasing to 40 °C. After the reaction is complete as determined by TLC, the mixed aqueous solution was extracted with ethyl acetate  $(25 \text{ mL} \times 5)$  and then the solvent was removed under vacuum to yield 0.12 g TNHA as a yellow solid in a yield of 19.6%. <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>) δ: 4.74 (d, 2H), 5.21 (dd, 2H), 5.66 (d, 1H), 6.92 (d, 1H);  $^{13}$ C NMR (125 MHz, acetone- $d_6$ )  $\delta$ : 50.72, 59.67, 95.04. IR (KBr, v/cm): 3441, 2924, 2139, 1566, 1420, 1296, 1244, 950, 754; Anal. Calcd for C<sub>4</sub>H<sub>6</sub>N<sub>8</sub>O<sub>6</sub> (%): C

18.32, H 2.29, N 42.75. Found C 18.27, H 2030, N 42.82. *m*/*z*: 262.0293.

5-Fluoro-1,3,5-trinitrohexahydropyrimidine (TNHF). The stirred solution of TNHP (0.5 g, 2.26 mmol) in methanol (10 mL) was added dropwise to another solution of potassium hydroxide in methanol (10 mL) for 5 min at 20 °C. On completion of the addition, the mixed solution was stirred at ambient temperature overnight and then the solvent removed in a vacuum. The resulting solid was washed with ethyl acetate several times and a yellow solid (0.47 g, 1.82 mmol) was obtained. 0.88 g of the solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (35 mL) at room temperature with vigorous stirring for 10 min. And Selectfluor® (2.42 g, 6.84 mmol) was added slowly to the mixture, stirred for 2 days, and then the solvent was removed under vacuum to obtain some yellow solid. The residual was extracted with ethyl acetate (25 mL  $\times$  3). Then, a pale yellow solid, 5-fluoro-1,3,5-trinitrohexahydropyrimidine (0.16 g), was obtained from the extracted solution by column chromatography in a yield of 20.06%. <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$ : 4.23 (dd, 1H), 4.97 (dd, 1H), 5.28 (m, 3H), 7.03 (m, 1H); <sup>13</sup>C NMR (125 MHz, acetone- $d_6$ )  $\delta$ : 51.30, 59.84, 82.43; <sup>19</sup>F NMR (500 MHz, acetone- $d_6$ )  $\delta$ : 95.04. IR (KBr,  $\nu$ /cm): 3433, 3044, 1577, 1450, 1292, 1258, 1013, 891, 754; Anal. Calcd for C<sub>4</sub>H<sub>6</sub>FN<sub>5</sub>O<sub>6</sub> (%): C 20.08, H 2.51, N 29.29. Found C 20.28, H 2.62, N 29.27. m/z: 239.2305.

## Author contributions

Kaidi Yang carried out the synthetic work and performance experiments of the research. Fuqiang Bi and Bozhou Wang designed the synthetic strategies and corresponding experimental conditions. Junlin Zhang and Bozhou Wang designed the material structures and the performance studies. Kaidi Yang, Qi Xue, Huan Huo and Chao Bai carried out the analysis of the structures.

## Conflicts of interest

There are no conflicts to declare.

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