

1 Molecular Design of Long Intra-annular Nitrogen Chains : 3H- 2 tetrazolo[1,5-d]tetrazole-Based High-Energy-Density Materials

3 Xiuxiu ZHAO¹, Yingchao ZHANG¹, Congxia XIE¹, Long TAN^{2*}

4 ¹Key Laboratory of Eco-chemical Engineering, Ministry of Education

5 College of Chemistry and Molecular Engineering

6 Qingdao University of Science and Technology

7 Qingdao, 266042 (P.R. China)

8 ²College of Electromechanical Engineering

9 Qingdao University of Science and Technology

10 Qingdao, 266042 (P.R. China)

11 *Corresponding author

12 E-mail addresses: tanlong029@163.com

13 Abstract

14 Energetic compounds containing long nitrogen chain, have been a research hotspot. Fused
15 heterocycles are stable due to their aromatic systems. The compound obtained by combining long
16 nitrogen chain and fused ring can not only retain good energetic property, but also ensure better
17 stability. This work designed eight fused heterocycle-based energetic compounds, 3H-
18 tetrazolo[1,5-d]tetrazole (**1**) and its derivatives (**2-8**), containing a nitrogen chain with seven
19 nitrogen atoms. The HOF, thermal stability, and energetic properties of these compounds were
20 studied by using the DFT method. The results show that the introduction of -NO₂, -N₃, -NF₂, -
21 ONO₂, -NHNO₂ groups increased the density, HOF, detonation velocity, and detonation pressure
22 greatly. The densities of **3**, **5**, **7**, and **8** fall within the range designated for high-energy-density
23 materials. The calculated detonation velocity of the compounds **3** and **8** are up to 9.86 km s⁻¹ and
24 9.78 km s⁻¹, which are superior to that of CL-20. The kinetic study of the thermal decomposition
25 mechanism indicates that the N-R bonds maybe not the weakest bonds of these compounds. The
26 tetrazole ring opening of the heterocycle-based energetic compounds, followed by N₂ elimination
27 is predicted to be the primary decomposition channel, whether or not they have substituent groups.

28 **KEYWORDS:** energetic compounds, fused heterocycles, nitrogen chain, thermal stability

29 Introduction

30 Energetic materials have been widely used in explosives, propellants and pyrotechnic agents. The
31 development of high-performance, high-density, high-stability and environmentally friendly
32 energetic materials has been a focus in recent years. Nitrogen-rich heterocyclic compounds are
33 rich in high-energy chemical bonds such as N=N, N-N, C-N, N-O and large ring tension, so they
34 have high heat of formation. The high-nitrogen and low-carbon structure makes it easier for them
35 to achieve oxygen balance. And most of the explosion products of the nitrogen-rich heterocyclic
36 compounds are N₂, which is friendly to the environment. So they are one of the most promising
37 high-energy-density materials (HEDMs).^[1-3]

38 The heat of formation of nitrogen-rich heterocyclic compounds is related to the nitrogen content
39 and the connection mode of the nitrogen atoms. The heat of formation increased with the increase
40 of nitrogen content and the number of directly connected nitrogen atoms.^[4-7] The commonly used
41 method to obtain long nitrogen chain is to oxidize the N-NH₂ moiety of nitrogen heterocycle to
42 form a tetrazene structure (N=N-N=N). Such growth of catenated nitrogen atom chains mainly
43 occurs between two heterocycles (inter-annular nitrogen chains).^[8-10] As the nitrogen chain in the
44 molecule becomes longer and longer, the detonation performance of this compound gets higher
45 and higher, but its stability gets worse and worse. When the length of the nitrogen chain grows to
46 eleven nitrogen atoms, the compound cannot be stable at room temperature.^[11] Stability limits the
47 further growth of the nitrogen chain. In this context, the development of long nitrogen chain
48 energetic compounds with high stability is extremely desirable.

49 Fused heterocycles are stable due to their aromatic systems. The compound obtained by
50 combining long nitrogen chain and fused ring can not only retain good energetic property, but also
51 ensure better stability. Such growth of catenated nitrogen atom chains occurs within two
52 heterocycles (intra-annular nitrogen chains). Fused heterocycles with additional ring strain energy
53 can be used as high-performance explosives.^[12-14] In 1977, Paudler et al. synthesized tetrazolo[1,5-
54 b][1,2,4]triazine (N5 chain).^[15] Then Willer et al. improved the synthesis method of tetrazolo[1,5-
55 b][1,2,4] triazine.^[16] Taha reported the synthesis of 3H-tetrazolo[1,5-d]tetrazole (N7 chain) in 2005.
56 ^[17] These studies were mainly focused on the synthesis of fused heterocycles with long nitrogen
57 chain. There was no further research on their energetic properties. Xiao Heming et al. designed
58 tetrazolo[1,5-b][1,2,4,5]tetrazine and its derivatives (N5 chain) in 2010. They calculated the heats
59 of formation (HOFs) and energetic performance of these compounds.^[18] The density and
60 detonation performance of the compound, obtained by introducing the energetic group -N(NO₂)₂
61 into tetrazolo[1,5-b][1,2,4,5]tetrazine, exceed those of HMX.^[19] These studies show that fused
62 heterocycles with long nitrogen chain have the potential to become candidates of HEDMs. Thus, it
63 is significant to search for longer nitrogen atom chains in fused heterocycles. Nowadays, computer
64 tests become an effective way to design high-energy-density compounds theoretically. Theoretical
65 studies not only make it possible to screen candidate compounds, but also provide understanding
66 in terms of the relationships between molecular structure and property.^[20-21]

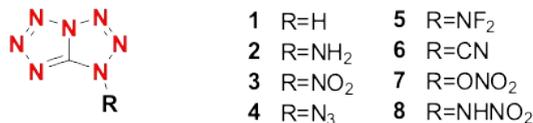
67 In this work, we designed eight fused heterocycle-based energetic compounds (**1-8**), containing a
68 nitrogen chain connected by seven nitrogen atoms (N7 chain), via the construction of the fused
69 ring skeleton and subsequent improvements in their energetic performance by adding energetic
70 groups to the backbones. The density, heat of formation (HOF), and thermal stability of these
71 compounds were studied by using density functional theory (DFT) method. The HOFs were
72 calculated by designingisodesmic reactions. Their detonation velocities and pressures were
73 calculated with EXPLO5 v6.01.^[22] In particular, considering this problem that the application of an
74 energetic compound containing a long nitrogen chain is strongly determined by its thermal
75 stability, we gave a detailed kinetic study of the decomposition mechanism of the designed fused
76 heterocycle-based energetic compounds. It is expected that our results can provide valuable
77 information to figure out what key factors could affect the stability of these compounds, but also
78 contribute to rational design of longer intra-annular nitrogen chains.

79 **Methods**

80 **Molecular design**

81 We chose 3H-tetrazolo[1,5-d]tetrazole (**1**) as the parent compound. Introduce -NH₂, -NO₂, -N₃, -
82 NF₂, -CN, -ONO₂, -NHNO₂ energetic groups on the nitrogen atom of compound **1** to obtain
83 compounds **2-8**, respectively.

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Figure 1. 3H-tetrazolo[1,5-d]tetrazole and its derivatives

87 **Calculation details**

88 The method of isodesmic reactions with hybrid DFT-B3LYP^[23-24] has been successfully employed
89 to predict the HOFs of energetic compounds.^[25-27] Considering the weak interaction in the
90 compounds, the DFT-B3LYP and DFT-wB97XD^[28] methods were adopted for comparison
91 calculation. To reduce the calculation errors of HOFs, we designed isodesmic reactions where the
92 numbers of all kinds of bonds were kept unchanged, and the big molecules were converted into
93 small ones while the basic skeleton of 3H-tetrazolo[1,5-d]tetrazole keeps invariable. The designed
94 isodesmic reactions are given in the Supplementary Information. Structural optimization and
95 vibration frequency calculations were performed at B3LYP/6-311G** and wB97XD/6-311G**
96 levels, respectively.^[29-30] In order to obtain more accurate total energies (E_0), the E_0 values were
97 also calculated at B3LYP/def2-TZVP and wB97XD/def2-TZVP levels respectively.^[31] The CBS-
98 QB3^[32], CBS-Q^[33], G2^[34] and G3MP2B3^[35] methods were used to calculate the HOFs of small
99 molecules. The detailed results were shown in the Supplementary Information.

100 Thermal decomposition simulation is an effective way to study the factors affecting the thermal
101 stability of energetic compounds.^[36-37] The keyword opt = TS is used to search for the transition
102 state (TS) of the designed compounds at B3LYP/6-311G** level. It is proved by frequency
103 calculations that all transition states (TSs) have only one imaginary frequency, and its vibrational
104 mode connects the directions of reactants and products. The rationally of the TS was verified by
105 Intrinsic Reaction Coordinates (IRC) theory. The TS, reactants and products are located in the
106 same IRC path, which has the lowest energy on the potential energy surface.^[38] The free energy
107 barrier of thermal decomposition reaction at 298K can be calculated by the following formulas:

108
$$\Delta G_{298K} = \sum G_{f,P} - \sum G_{f,R} \quad (3)$$

109
$$G_{298K} = H_{298K} - T * S = E_0 + ZPE + H_T - T * S \quad (4)$$

110 where $G_{f,P}$ and $G_{f,R}$ are the HOFs of the products and reactants at 298 K, respectively. E_0 is total
111 energy of molecule at 0 K, ZPE is zero-point energy, and H_T is thermal correction from 0 K to 298
112 K.

113 Structural optimization and vibration frequency calculations were performed with the Gaussian
114 09 package.^[39] Using the default convergence criteria in the program, the optimization were
115 performed without any symmetry constraints. All optimized structures are at the energy minimum
116 point on the potential energy surface without imaginary frequency. The detonation velocities (D)
117 and detonation pressures (P) of the designed energetic compounds were evaluated by EXPLO5 v

118 6.01 software.^[22]

119 Results and discussion

120 The physicochemical and energetic properties of the compounds **1-8** were shown in table 1. The
121 comparison for density, HOF, detonation velocity and detonation pressure of **1-8**, RDX, HMX,
122 and CL-20 is present in figure 2.

123 **Table 1** Physicochemical and energetic properties of compounds **1-8**, RDX, HMX, and CL-20

| compound | N ^a | OB ^b | ρ^c | $\Delta H_{f,solid}^d$ | D ^e | P ^f |
|--------------------|----------------|-----------------|----------|------------------------|----------------|----------------|
| 1 | 88.3 | -36.01 | 1.71 | 641.36 | 9.05 | 31.25 |
| 2 | 88.9 | -38.07 | 1.67 | 736.20 | 9.21 | 32.22 |
| 3 | 71.8 | 0.00 | 1.86 | 757.27 | 9.86 | 41.77 |
| 4 | 92.1 | -21.04 | 1.75 | 1129.54 | 9.50 | 36.66 |
| 5 | 69.1 | -9.87 | 1.97 | 731.79 | 9.16 | 38.44 |
| 6 | 82.3 | -47.03 | 1.70 | 877.98 | 8.35 | 26.53 |
| 7 | 65.1 | 9.30 | 1.88 | 735.95 | 9.59 | 39.66 |
| 8 | 73.7 | -4.68 | 1.82 | 781.38 | 9.78 | 40.72 |
| RDX ^g | 37.8 | -21.61 | 1.81 | 86.3 | 8.87 | 34.80 |
| HMX ^g | 37.8 | -21.62 | 1.90 | 116.1 | 9.26 | 39.40 |
| CL-20 ^g | 38.3 | -10.95 | 2.04 | 365.4 | 9.73 | 44.4 |

a Nitrogen content (%). b Oxygen balance (OB = (xO-2yC-1/2zH)1600/M) (%). c Calculated density (g cm⁻³).

d Calculated enthalpy of formation (kJ mol⁻¹). e Detonation velocity (km s⁻¹). f Detonation pressure (GPa). g

124 **Nitrogen content (N) and Oxygen balance (OB)**

125 Obviously, because of the long nitrogen chain, these fused heterocycle-based energetic compounds
126 have high nitrogen contents ranging from 65.1% (**7**) to 92.1% (**4**), which are much higher than
127 those of the commonly used high explosives such as RDX (N: 37.8%), HMX (N: 37.8%), and CL-
128 20 (N: 38.3%). Compared to the parent compound **1**, the introduction of -NH₂ and -N₃ groups can
129 effectively increase the nitrogen content of these compounds. The nitrogen content of compound **4**
130 is up to 92.1%. Oxygen balance (OB), an expression used to indicate the degree to which an
131 explosive can be oxidized, is an important index for identifying the potential of energetic materials
132 as explosives or oxidants. Compound **7** possesses positive oxygen balance at 9.30%, and
133 compound **3** possesses zero oxygen balance. Most of the compounds have significantly higher
134 nitrogen content and higher OB, which are superior to those of RDX and HMX.

135 **Density**

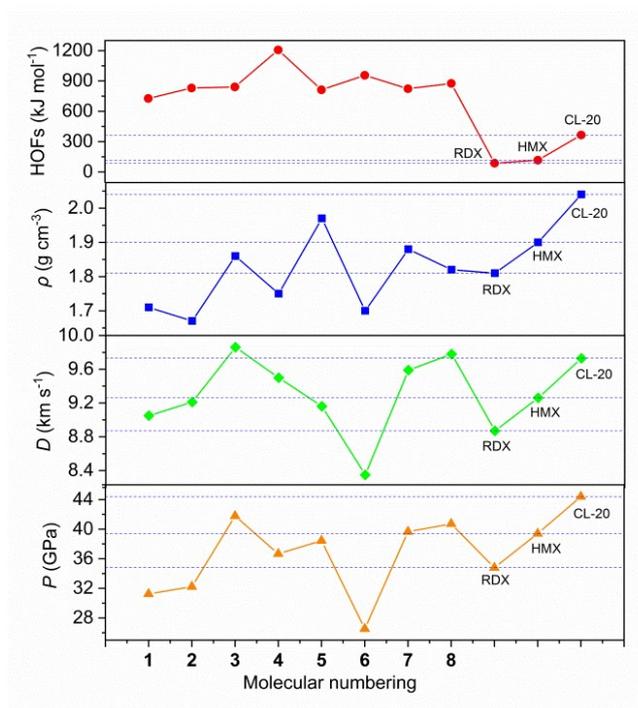
136 The calculated densities of the compounds **1–8** lie in the range of 1.67 to 1.97 g cm⁻³. The
137 introduction of -NO₂, -N₃, -NF₂, -ONO₂, -NHNO₂ significantly increased the density. Particularly,
138 the densities of **3** (1.86 g cm⁻³), **5** (1.97 g cm⁻³), **7** (1.88 g cm⁻³), and **8** (1.82 g cm⁻³) fall within the
139 range designated for high-energy-density materials (HEDMs, 1.8–2.0 g cm⁻³). And the densities of
140 the compounds **3**, **5**, **7**, and **8** are higher than that of RDX.

141 **Heat of formation**

142 The heats of formation (HOFs) for the compounds **1–8** are calculated with the density functional
143 theory (DFT) B3LYP method by means of designed isodemic and isogyric reactions. Detailed
144 calculation method is shown in the Supplementary Information. All of the HOFs of are shown in
145 table 1. All of the designed compounds have high positive HOFs, which are much higher than that
146 of CL-20. High HOF will contribute to the increase of detonation velocity and detonation
147 pressure. The introduction of -NH₂, -NO₂, -N₃, -NF₂, -CN, -ONO₂, -NHNO₂ energetic groups
148 increased the heat of formation greatly.

149 **Detonation properties**

150 Based on the calculated heats of formation and densities, the detonation properties of these fused
151 heterocycle-based compounds were evaluated with EXPLO5 v6.01. As shown in table 1, the
152 detonation velocity of compounds **1–8** are in the range of 8.35 km s⁻¹ (**6**) to 9.86 km s⁻¹ (**3**); the
153 detonation pressures of compounds **1–8** are in the range of 26.53 GPa (**6**) to 41.77 GPa (**3**). Most
154 of these compounds exhibit excellent explosive properties, which are superior to those of RDX
155 and HMX. The calculated detonation velocity of the compounds **3** and **8** are up to 9.86 km s⁻¹ and
156 9.78 km s⁻¹, which are superior to that of CL-20 (9.73 km s⁻¹). Compared to the parent compound
157 **1**, the introduction of energetic groups, except -CN, result in a significant increase in the explosive
158 properties of these fused heterocycle-based compounds.



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Figure 2. The comparison for density, HOF, P and D of **1-8**, RDX, HMX, and CL-20

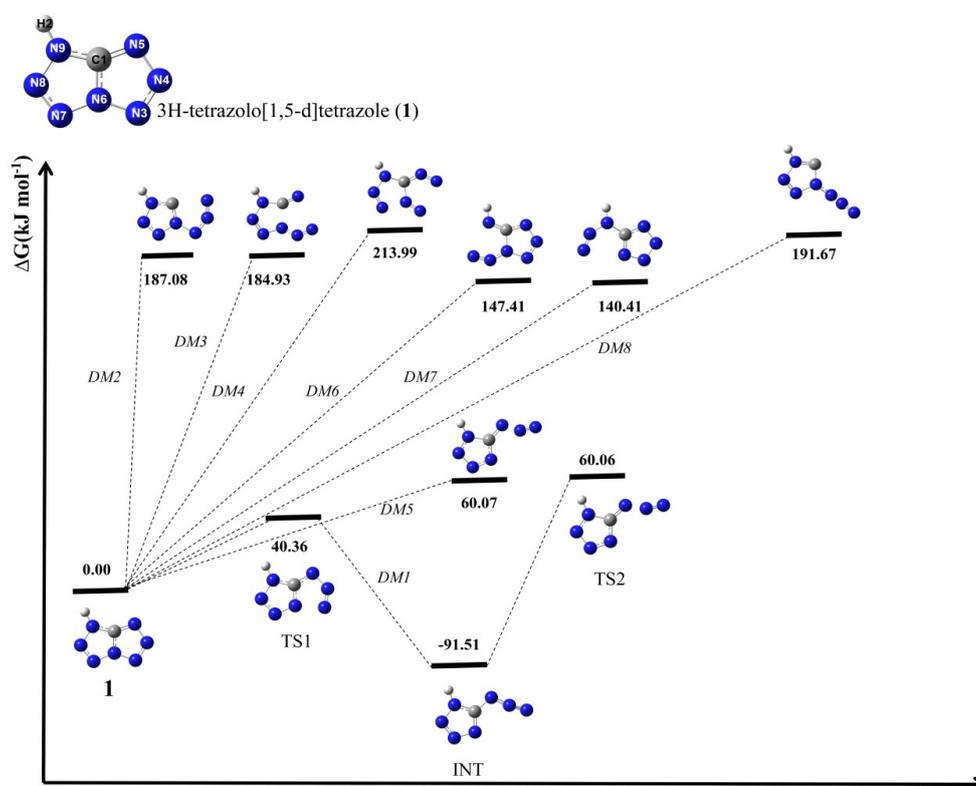
161 **Thermal stability**

162 The application of energetic compounds is strongly determined by their thermal stability. Bond
 163 dissociation energy (BDE) for the weakest bond of a compound usually provides useful
 164 information for understanding the stability of a compound. So we calculated the bond dissociation
 165 energy (BDE) for N-R of the compounds **2-8** at the B3LYP/6-311G** level to understand the
 166 stability of these fused heterocycle-based compounds. The BDEs are listed in table 2. The BDE
 167 values for N-NH₂, N-NO₂, N-N₃, N-NF₂, N-CN, N-ONO₂, N-NHNO₂ of the compounds **2-8** are
 168 218.42 kJ mol⁻¹, 41.06 kJ mol⁻¹, 107.82 kJ mol⁻¹, 60.34 kJ mol⁻¹, 359.16 kJ mol⁻¹, 96.87 kJ mol⁻¹,
 169 and 177.30 kJ mol⁻¹ respectively. According to the values, it can be deduced that the thermal
 170 stability of **6** is the highest among the compounds **2-8**, while the thermal stability of **3** is the
 171 lowest.

172 In order to study the influence of substituent groups on the thermal stability of these fused
 173 heterocycle-based compounds, it is necessary to understand the energy required for the
 174 decomposition of compound **1**. However, the initial step should be via ring cleavage in thermal
 175 decompositions for compound **1**. The ring-opening reaction may be the rupture of a single bond or
 176 multiple bonds at the same time. Using BDE to judge the thermal stability of compound **1** may
 177 cause large errors. Therefore, we carried out kinetic study of compound **1**. We explored eight
 178 decomposition pathways. These decomposition mechanisms are illustrated in figure 3 and include:
 179 (1) The dissociation of N3-N6 bond goes ahead through the right tetrazole ring-opening transition
 180 state TS1, with a reaction barrier of 40.36 kJ mol⁻¹, which is confirmed by IRC calculation. Then
 181 the N4-N5 bond breaks, releasing nitrogen gas (*DM1*). (2) The dissociation of C1-N5 bond goes
 182 ahead through the right tetrazole ring-opening transition state TS1, with a reaction barrier of
 183 187.08 kJ mol⁻¹ (*DM2*). (3) The dissociations simultaneously of C1-N6 and N4-N5 bonds go

184 ahead through the two tetrazole rings-opening transition state TS1, with a reaction barrier of
 185 184.93 kJ mol⁻¹ (DM3). (4) The dissociations simultaneously of N3-N4 and N6-N7 bonds go
 186 ahead through the two tetrazole rings-opening transition state TS1, with a reaction barrier of
 187 213.99 kJ mol⁻¹ (DM4). (5) The dissociations simultaneously of N3-N6 and N4-N5 bonds go
 188 ahead through the right tetrazole ring-opening transition state TS1, releasing nitrogen gas, with a
 189 reaction barrier of 60.07 kJ mol⁻¹ (DM5). (6) The dissociation of N8-N9 bond goes ahead through
 190 the left tetrazole ring-opening transition state TS1, with a reaction barrier of 147.41 kJ mol⁻¹
 191 (DM6). (7) The dissociation of N6-N7 bond goes ahead through the left tetrazole ring-opening
 192 transition state TS1, with a reaction barrier of 140.41 kJ mol⁻¹ (DM7). (8) The dissociations
 193 simultaneously of C1-N5 and N3-N4 bonds go ahead through the right tetrazole ring-opening
 194 transition state TS1, releasing nitrogen gas, with a reaction barrier of 191.67 kJ mol⁻¹ (DM8).
 195 Compared the energy required for the initial decomposition step, *DMI* is the most likely
 196 decomposition pathway.

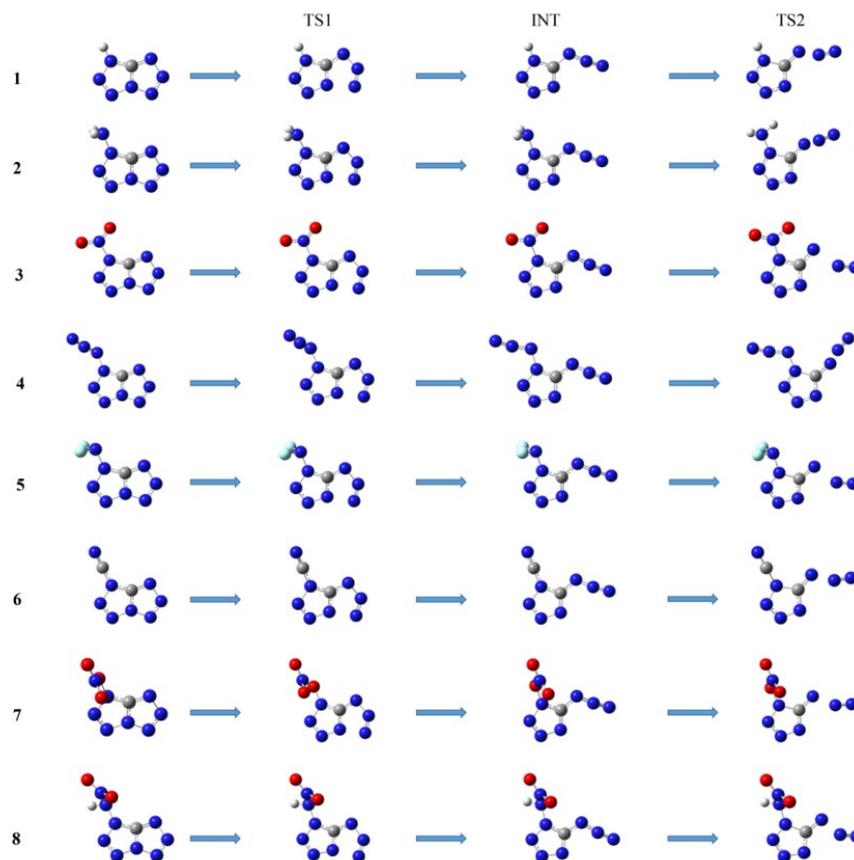
197 Using the same method, we carried out kinetic study of compounds **2-8**. Each compound has
 198 eight possible thermal decomposition pathways, which are similar to the eight decomposition
 199 pathways of compound **1**. The most likely decomposition pathway of compounds **2-8** is that the
 200 dissociation of N3-N6 bond, followed by the rupture of N4-N5 and nitrogen gas release, which is
 201 the same with the *DMI* of compound **1**. The introduction of substituent groups does not change
 202 the most likely decomposition pathway of these fused heterocycle-based compounds. The most
 203 likely decomposition pathways of compounds **1-8** are shown in figure 4. The energies required for
 204 the most likely decomposition pathways of compounds **2-8** are listed in table 2.



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Figure 3. The possible decomposition pathways of compound 1



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Figure 4. The most likely decomposition pathways of compounds **1-8**

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Interestingly, the energies required for the most likely decomposition pathway of compounds **2-8** are lower than the BDEs for N-R bonds of compounds **2-8**. The N-R bonds maybe not the weakest bonds of these compounds. According to the kinetic studies, the decompositions of these compounds start from the opening of the tetrazole ring. Compared to the energy required for the most likely decomposition pathway of parent compound **1**, the introduction of -NH₂ group is beneficial to enhance thermal stability, while the introduction of other groups is not conducive to improve the thermal stability. It is worth noting that the BDE (41.06 kJ mol⁻¹) for N-NO₂ bond of compound **3** is almost the same as the energy required for the most likely decomposition pathway of compound **3** (40.19 kJ mol⁻¹). For compound **3**, there may be two decomposition pathways. One way of decomposition is the breaking of N-NO₂ bond. Another way of decomposition is the opening of the tetrazole ring at the N3-N6 bond. The most likely decomposition pathway of compounds **1, 2**, and **4-8** is that the dissociation of N3-N6 bond, followed by the rupture of N4-N5 and nitrogen gas release.

Table 2 BDEs (kJ mol⁻¹) for N-R of **2-8** and predicted energy required (kJ mol⁻¹) for the decomposition of **1-8**

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|-----|----------|----------|----------|----------|----------|----------|----------|----------|
| BDE | | 218.42 | 41.06 | 107.82 | 60.34 | 359.16 | 96.87 | 177.30 |

| | | | | | | | | |
|-------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| Predicted energy requirements | 40.36 | 40.90 | 40.19 | 37.76 | 37.46 | 35.73 | 39.30 | 38.02 |
|-------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|

223 Conclusions

224 In this work, we designed eight new fused heterocycle-based energetic compounds via the
225 construction of the fused ring skeleton and subsequent improvements in their energetic
226 performance by adding energetic groups to the backbones. Nitrogen content, oxygen balance,
227 density, HOFs, detonation velocity, and detonation pressure of these compounds were calculated.
228 The results show that most of the compounds have significantly higher nitrogen content and
229 higher OB, which are superior to those of RDX and HMX. Compared to the parent compound **1**,
230 the introduction of -NO₂, -N₃, -NF₂, -ONO₂, -NHNO₂ energetic groups increased the heat of
231 formation, detonation velocity, and detonation pressure greatly. The kinetic study of the thermal
232 decomposition mechanism indicates that the N-R bonds maybe not the weakest bonds of these
233 compounds. The tetrazole ring opening of the heterocycle-based energetic compounds, followed
234 by N₂ elimination is predicted to be the primary decomposition channel, whether or not they have
235 substituent groups. Considering the detonation performance and thermal stability, the compounds
236 **3**, **7**, and **8** may be regarded as potential candidates of HEDMs. These results provide basic
237 information for the molecular design of novel HEDMs.

238 Conflicts of interest

239 There are no conflicts to declare.

240 Funding Information

241 The authors gratefully acknowledge the financial support from the National Natural Science
242 Foundation of China (Grant No. 21805153 and 52005276) and the Natural Science Foundation of
243 Shandong Province (Grant No. ZR2018BA019 and ZR2020QE174).

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