

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

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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]

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

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

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

Methods

Molecular design

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

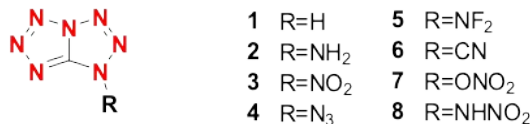


Figure 1. 3H-tetrazolo[1,5-d]tetrazole and its derivatives

Calculation details

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

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

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

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

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

Structural optimization and vibration frequency calculations were performed with the Gaussian 09 package.^[39] Using the default convergence criteria in the program, the optimization were performed without any symmetry constraints. All optimized structures are at the energy minimum point on the potential energy surface without imaginary frequency. The detonation velocities (D) 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

Nitrogen content (N) and Oxygen balance (OB)

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

Density

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

Heat of formation

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

Detonation properties

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

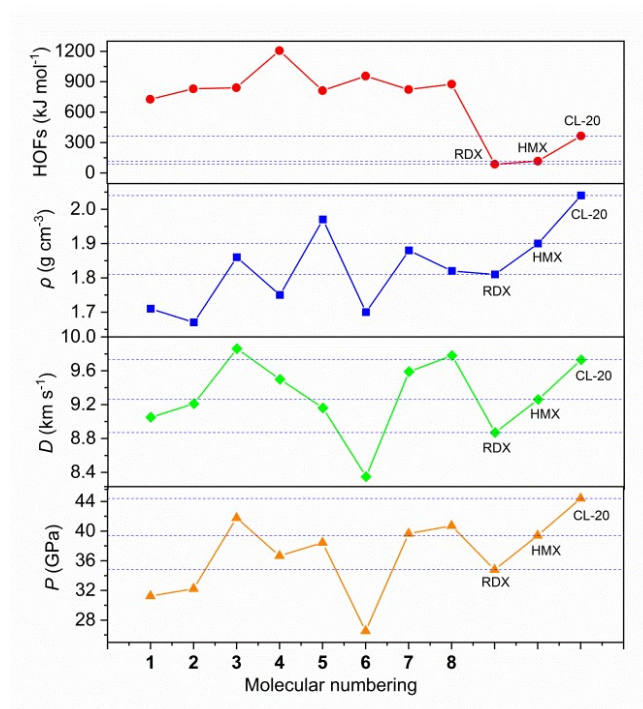


Figure 2. The comparison for density, HOF, P and D of **1-8**, RDX, HMX, and CL-20

Thermal stability

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

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

ahead through the two tetrazole rings-opening transition state TS1, with a reaction barrier of 184.93 kJ mol⁻¹ (DM3). (4) The dissociations simultaneously of N3-N4 and N6-N7 bonds go ahead through the two tetrazole rings-opening transition state TS1, with a reaction barrier of 213.99 kJ mol⁻¹ (DM4). (5) The dissociations simultaneously of N3-N6 and N4-N5 bonds go ahead through the right tetrazole ring-opening transition state TS1, releasing nitrogen gas, with a reaction barrier of 60.07 kJ mol⁻¹ (DM5). (6) The dissociation of N8-N9 bond goes ahead through the left tetrazole ring-opening transition state TS1, with a reaction barrier of 147.41 kJ mol⁻¹ (DM6). (7) The dissociation of N6-N7 bond goes ahead through the left tetrazole ring-opening transition state TS1, with a reaction barrier of 140.41 kJ mol⁻¹ (DM7). (8) The dissociations simultaneously of C1-N5 and N3-N4 bonds go ahead through the right tetrazole ring-opening transition state TS1, releasing nitrogen gas, with a reaction barrier of 191.67 kJ mol⁻¹ (DM8). Compared the energy required for the initial decomposition step, DM1 is the most likely decomposition pathway.

Using the same method, we carried out kinetic study of compounds **2-8**. Each compound has eight possible thermal decomposition pathways, which are similar to the eight decomposition pathways of compound **1**. The most likely decomposition pathway of compounds **2-8** is that the dissociation of N3-N6 bond, followed by the rupture of N4-N5 and nitrogen gas release, which is the same with the DM1 of compound **1**. The introduction of substituent groups does not change the most likely decomposition pathway of these fused heterocycle-based compounds. The most likely decomposition pathways of compounds **1-8** are shown in figure 4. The energies required for the most likely decomposition pathways of compounds **2-8** are listed in table 2.

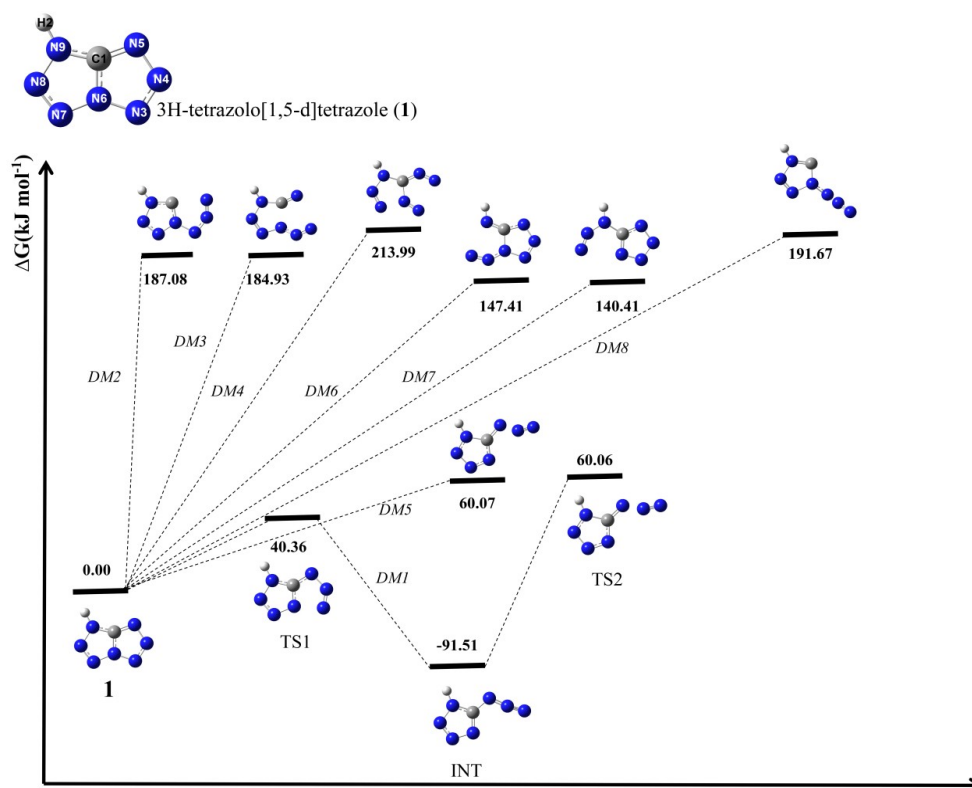


Figure 3. The possible decomposition pathways of compound **1**

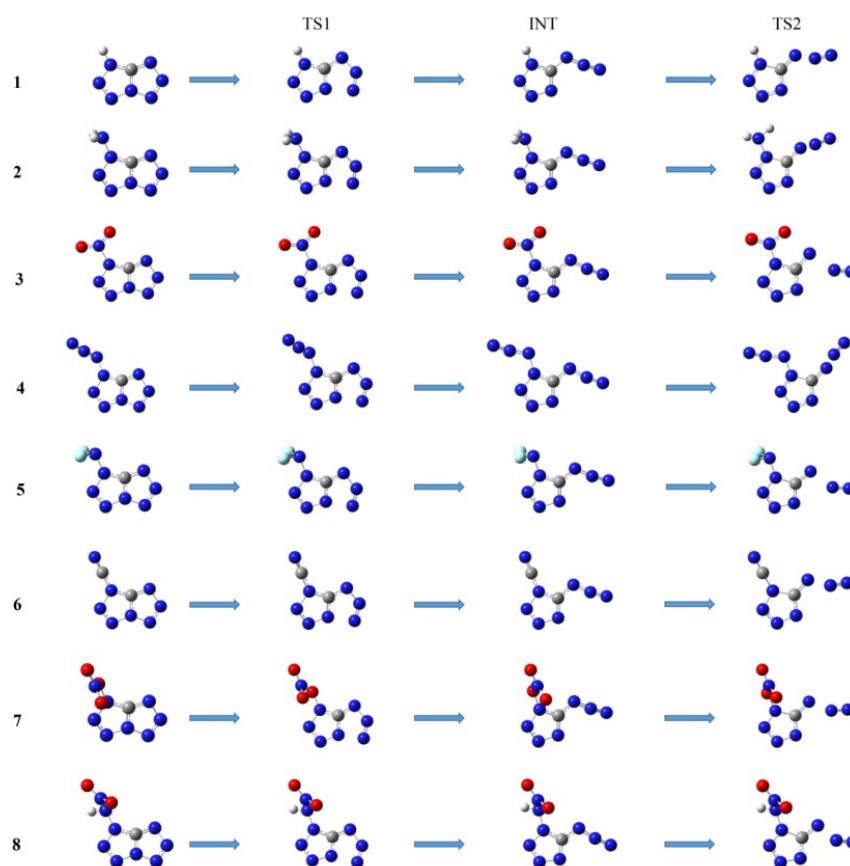


Figure 4. The most likely decomposition pathways of compounds **1-8**

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
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Conclusions

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

Conflicts of interest

There are no conflicts to declare.

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References

- [1] P. Yin, C. L. He, J. M. Shreeve, *J. Mater. Chem. A* 2016, **4**, 1514.
- [2] J. H. Zhang, J. M. Shreeve, *J. Am. Chem. Soc.* 2014, **136**, 4437.
- [3] D. Kumar, G. H. Imler, D. A. Parrish, J. M. Shreeve, *Chem. Eur. J.* 2017, **23**, 1743.
- [4] T. P. Kofman, *Russ. J. Org. Chem.* 2002, **38**, 1231.
- [5] T. M. Klapötke, C. M. Sabaté, *Chem. Mater.* 2008, **20**, 3629.
- [6] G. Hervé, C. Roussel, H. Graindorge, *Angew. Chem. Int. Ed.* 2010, **49**, 3177.
- [7] T. M. Klapötke, B. Krumm, F. A. Martin, J. Stierstorfer, *Chem. Asian J.* 2012, **7**, 214.
- [8] Y. C. Li, C. Qi, S. H. Li, H. J. Zhang, C. H. Sun, Y. Z. Yu, S. P. Pang, *J. Am. Chem. Soc.* 2010, **132**, 12172.
- [9] T. M. Klapötke, D. G. Piercey, J. Stierstorfer, *Dalton Trans.* 2012, **41**, 9451.
- [10] T. M. Klapötke, D. G. Piercey, *Inorg. Chem.* 2011, **50**, 2732.
- [11] Y. X. Tang, H. W. Yang, B. Wu, X. H. Ju, C. X. Lu, G. B. Cheng, *Angew. Chem.* 2013, **125**,

257 4975.

258 [12] J. H. Zhang, D. A. Parrish, J. M. Shreeve, *Chem. Asian J.* 2014, **9**, 2953.

259 [13] V. Thottempudi, F. Forohor, D. A. Parrish, J. M. Shreeve, *Angew. Chem. Int. Ed.* 2012, **51**,
 260 9881.

261 [14] D. G. Piercey, D. E. Chavez, B. L. Scott, G. H. Imler, D. A. Parrish, *Angew. Chem.* 2016, **128**,
 262 15541.

263 [15] M. M. Goodman, W. W. Paudler, *J. Org. Chem.* 1977, **42**, 1866.

264 [16] R. L. Willer, R. A. Henry, *J. Org. Chem.* 1988, **53**, 5371.

265 [17] M. A. M. Taha, *J. Indian Chem. Soc.* 2005, **36**, 172.

266 [18] X. H. Jin, B. C. Hu, Z. L. Liu, *Struct. Chem.* 2015, **26**, 401.

267 [19] N. Fischer, D. Fischer, T. M. Klapotke, D. G. Piercey and J. Stierstorfer, *J. Mater. Chem.*
 268 2012, **22**, 20418.

269 [20] X. H. Jin, B. C. Hu, Z. L. Liu, *Struct. Chem.* 2015, **26**, 401.

270 [21] S. Naserifar, S. Zybin, C. C. Ye, W. A. Goddard, *J. Mater. Chem. A* 2016, **4**, 1264.

271 [22] M. Sućeska, EXPLO5 V6. 01; Brodarski Institute: Zagreb, Croatia, 2012.

272 [23] A. D. Becke, *Phys. Rev. A* 1988, **38**, 3098.

273 [24] A. D. Becke, *J. Chem. Phys.* 1996, **104**, 1040.

274 [25] R. U. Khan, S. M. Zhu, W. H. Zhu, *J. Mol. Model.* 2019, **25**, 283.

275 [26] T. Wei, W. H. Zhu, X. W. Zhang, Y. F. Li, H. M. Xiao, *J. Phys. Chem. A* 2009, **113**, 9404.

276 [27] X. W. Zhang, W. H. Zhu, H. M. Xiao, *J. Phys. Chem. A* 2010, **114**, 603.

277 [28] J. D. Chai, M. H. Gordon, *Phys. Chem. Chem. Phys.* 2008, **10**, 6615.

278 [29] R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.* 1980, **72**, 650.

279 [30] B. P. Pritchard, D. Altarawy, B. Didier, T. D. Gibson, T. L. Windus, *J. Chem. Inf. Model.*
 280 2019, **59**, 4814.

281 [31] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, **7**, 3297.

282 [32] J. A. Montgomery Jr., M. J. Frisch, J. W. Ochterski, *J. Chem. Phys.* 2000, **112**, 6532.

283 [33] J. A. Montgomery Jr., M. J. Frisch, *J. Chem. Phys.* 1999, **110**, 2822.

284 [34] L. A. Curtiss, K. Raghavachari, G. W. Trucks, J. A. Pople, *J. Chem. Phys.* 1991, **94**, 7221.

285 [35] A. G. Baboul, L. A. Curtiss, P. C. Redfern, K. Raghavachari, *J. Chem. Phys.* 1999, **110**, 7650.

286 [36] C. C. Ye, Q. An, W. A. Goddard III, T. Cheng, W. G. Liu, S. V. Zybin, X. H. Ju, *J. Mater.*
 287 *Chem. A* 2015, **3**, 1972.

288 [37] V. G. Kiselev, P. B. Cheblakov, N. P. Gritsan, *J. Phys. Chem. A* 2011, **115**, 1743.

289 [38] K. Fukui, *Acc. Chem. Res.* 1981, **14**, 363.

290 [39] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A.
 291 Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M.
 292 Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada,
 293 M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H.
 294 Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E.
 295 Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A.
 296 Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E.
 297 Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev,
 298 A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G.
 299 Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B.
 300 Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

- 301 [40] P. Plitzer, J. S. Murray, M. E. Grice, *Mol. Phys.* 1997, **91**, 923.
302 [41] E. F. Byrd, B. M. Rice, *J. Phys. Chem. A* 2006, **110**, 1005.
303 [42] T. Lu, F. W. Chen, *J. Comput. Chem.* 2012, **33**, 580.
304 [43] J. Zhang, *J. Chem. Theory Comput.* 2018, **14**, 572.
305 [44] R. L. David, Handbook of Chemistry and Physics, 84th ed., CRC Press, 2003-2004, Sect 5.
306 [45] H.Y. Afeefy, J.F. Liebman, S.E. Stein, Neutral thermochemical data, in: Linstrom P J, Mallard
307 W G(Eds.), NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National
308 Institute of Standards and Technology, Gaithersburg, MD, 2000, <http://webbook.nist.gov>.
309 [46] J. P. Merrick, D. Moran, L. Radom, *J. Phys. Chem. A* 2007, **111**, 11683.