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The enhanced properties of energetic materials through ring replacement strategy

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ABSTRACT

In order to meet the high demands of modern energetic materials, numerous routes have been explored by the researchers. In this study, a ring replacement strategy was designed to enhance the energetic properties. The ring replacement compounds **11** (N,N'-methylenebis (N-(4-(2H-tetrazol-5-yl)-1,2,5-oxadiazol-3-yl)- nitramide) and **15** (N,N'-ethylenebis (N-(4-(2H-tetrazol-5-yl)-1,2,5-oxadiazol-3-yl)-nitramide), in which the oxadiazole rings connected to the furazan backbone were replaced by tetrazole rings were characterized by x-ray single crystal diffraction and NMR (¹H, ¹³C, ¹⁵N). The results compounds show that the heats of formation and detonation performance of the replacement of compounds were significantly better than those of the precursor compounds, and the nitrogen content of compounds **11** and **15** were improved from 41.18% and 39.81% to54.9% and 53.08%, respectively, which belongs to the category of high nitrogen compounds. In a word, the ring replacement strategy in this work offers fresh routes for the improvement in properties of energetic materials.

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1. Introduction

Energetic materials play a significant role in both military and civilian fields, since Nobel invented dynamite. It has been attracting considerable interest over the past two centuries [1]. Generally speaking, the energy density higher, the volume of the energetic materials needed for application is smaller, therefore, endowing energetic materials with improved detonation properties has always been the developmental theme of energetic materials [2–4]. In the past decades, many strategies have been employed to improve the properties of energetic materials, for instance, introduction of more powerful energetic groups to replace original groups as substituents on the backbone [5–7], employing cage or ring with strain as the energetic backbone [8–11], and close

https://doi.org/10.1016/j.molstruc.2019.127358 0022-2860/© 2019 Elsevier B.V. All rights reserved. packaging via hydrogen-bonding interactions [12–14], as well as anion exchange in metal-organic framework [15]. Nevertheless, due to the increasing development and modern demands of energetic materials, more approaches to improve the energetic properties are desired.

Among the numerous heterocyclic compounds proposed for energetic materials, oxadiazole compounds, due to higher densities and better oxygen balance of their derivatives compared to those of imidazole, pyrazole and triazole, make them better choice (Fig. 1a) [16,17]. Especially for the bis-oxadiazole derivatives, which display very promising as alternative to replace current explosive. Such as the 3,3'-dinitramino-4,4'-bifurazane and its derivatives [18], derivatives of 3-nitroamino-4-(5-nitroamino-1,2,4-oxadiazol-3-yl) furazan [6]. On the other hand, tetrazole has a higher heat of formation and nitrogen content than other types of heterocycle-based compounds, which would lead to relatively environmentally benign decomposition products [19–21], and some compounds based on tetrazole have favorable energetic properties [22]. Therefore, one ring of the bis-oxadiazole compounds was replaced by tetrazole, the heat of formation, oxygen balance and density

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(a) Calculated gas-phase heats of formation (G2 atomization method)^{6,25,32} for oxadiazoles and azoles



(b) This work (A Ring Replacement Strategy Towards Energetic Materials with High Nitrogen Contents)

Fig. 1. (a) The calculated gas-phase heats of formation for small ring compounds; (b) The ring replacement strategy was employed in this work.

would reach up to be an excellent combination, and some of these reported compounds' properties do satisfy modern demand of energetic materials [23–25]. However, there are seldom reports employing ring replacement to introduce tetrazole into oxadiazole, and none of them studied the energetic properties between the precursor and replaced compounds comprehensively [26,27]. What's more, most of the tetrazole-oxadiazole compound were synthesized from the cyano-oxadiazole compound, which almost has no power, it limits the investigation of structure-property relationship between precursor and resulted compounds.

Recently, our group successfully incorporated 1,2,4-oxadiazole, a five-membered heterocyclic ring, into a furan ring and synthesized compounds with modest energetic performance [28]. To continue further exploration, we envisage that if the 1,2,4oxadiazole rings are replaced by tetrazole rings (Fig. 1b), the nitrogen content can be further improved. Moreover, the heat of formation of 1,2,4-oxadiazole is lower than 1,2,5-oxadiazole ring, and the heat of formation of tetrazole is higher than that of 1,2,5oxadiazole. Hence, the heat of formation, nitrogen content, and the properties of replaced compounds would be improved greatly compared to their precursors. The energetic properties of resulted compounds were investigated and compared with their precursors comprehensively in this study.

2. Experimental

2.1. Safety precautions

Although we have experienced no difficulties in the synthesis and characterization of these compounds, all the compounds investigated are potentially explosive materials. Therefore, manipulations must be carried out in a hood behind a safety shield. Eye protection and leather gloves must be worn all the time. During synthesis and characterization, mechanical actions involving scratching or scraping must be avoided. All of the energetic compounds must be synthesized only in small amounts.

2.2. General methods

¹H spectra were recorded on a 300 MHz nuclear magnetic resonance spectrometer operating at 300 MHz ¹³C NMR spectra were recorded on a 400 MHz nuclear magnetic resonance spectrometer operating at 100 MHz. The solvent were [d6]dimethylsulfoxide ([d6]DMSO) and [d4]methanol ([d4]CH₃DO) unless otherwise specified. ¹⁵N NMR spectra was recorded on a 400 MHz nuclear magnetic resonance spectrometer operating at 40.5 MHz. The melting and decomposition points were recorded on a NETZSCH STA 449F3 equipment at a scan rate of 5 °C min⁻¹, respectively. Infrared spectra were recorded by using KBr pellets. Densities were measured at toom temperature using a MicromeriticsAccupyc π 1340 gas pycnometer. Elemental analyses were obtained on an ElementarVario MICRO CUBE (Germany) elemental analyser. Impact and friction-sensitivity measurements were tested by employing a standard BAM Fallhammer and a BAM friction tester. The acknowledgements come at the end of an article after the conclusions and before the notes and references.

2.3. X-ray crystallography

The single-crystal X-ray diffraction data of 5 and 15 · CH₃OH

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were collected at 293 K using graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å) using omega scans from a Bruker CCD area detector diffractometer. Data collection and reduction were performed and the unit cell was initially refined using Bruker SMART software. The reflection data were also corrected for *LP* factors. The structure was solved by direct methods and refined by a leastsquares method on F^2 using the Bruker SHELXTL program. In these structures, the value of the Flack parameter did not allow the direction of the polar axis to be determined and Friedel reflections were then merged for the final refinement. Details of the data collection and refinement are given in Table S1.

2.4. Computational method

The gas phase heats of formation for all new neutral compounds were obtained using isodesmic reactions. The geometric optimization and frequency analysis of the structures were calculated using B3LYP function with $6-31 + G^{**}$ basis set. All of the optimized structures were checked to be true local energy minima on the potential energy surface without imaginary frequencies. Singlepoint energies based on the optimized structures were calculated at the MP2/6-311++G^{**} set. Atomization energies for the frame molecules or ions were obtained by employing the G2 *ab initio* method. The conversion of gas phase enthalpies to solid phase values for the neutral compounds was done by subtracting the empirical heat of sublimation obtained based on Trouton's rule. Detonation properties of new compounds were calculated by using EXPLO5 program. More calculation details can be found in the Electronic Supporting Information.

2.5. Synthesis

2.5.1. 4-Hydrazinofurazan-3-carboxylic acid (5)

The synthesis of compound 5 is similar to compound 2 [26]. 3nitro-4-(1,2,4-oxadiazol-3-yl)furazan (5), (1.83 g, 10 mmol) was dissolved in MeOH (20 ml), the mixture was heated to 40–45 °C and treated with 80% N₂H₄·H₂O(1.02 ml, 21 mmol) at this temperature, accompanying the reaction mixture becoming cloudy from transparent solution, after the exothermic effect ended, the mixture was stirred at 40–45 °C for 1 h, cooled to room temperature and the precipitate was filtered off and recrystallized from H₂O. Yield in 80%, light brown needles. For compound 5. ¹H NMR (DMSO-*d*₆, ppm): δ 7.23 (s, 1H), 5.84 (s, 2H), 5.72 (s, 2H), 4.47 (s, 2H); ¹³C NMR (DMSO-*d*₆, ppm): δ 158.52, 140.18, 136.37. IR (KBr) \tilde{v} : 3379, 3335, 3155, 1664, 1564, 1603, 1464, 1320, 1288, 1192, 955, 853, 802, 651, 418 cm⁻¹. Elemental analysis (%) for C₃H₇N₇O (183): calculated: C 22.93; H 4.49; N 62.40; found: C 22.41; H 3.89; N 62.44. CCDC number: 1567538.

2.5.2. 3-Nitro-4-(tetrazol-5-yl) furazan (7)

4-(Tetrazol-5-yl)furazan-3-aminie (3) (3) (0.765 g, 5 mmol) was added into the oxidation mixture of H₂O₂ and concentrated sulphuric acid at 50–60 °C, attention please, this step is exothermic and the temperature stay 50–60 °C not easily. After the exothermic effect ended, the reaction mixture was stirred at this temperature for 1 h, cooled to room temperature and treated with H₂O (about 50 ml). The product was extracted with CH₂Cl₂, the organic extract was washed with saturated brines two times, dried with anhydrous sodium sulphate evaporated in vacuum, the solid residue was recrystallized from MeOH. Yield 0.76 g (83%), white round-shaped crystals, Dec 215 °C. ¹H NMR (DMSO-*d*₆, ppm): δ 10.08 (s, 1H); ¹³C NMR (DMSO-*d*₆, ppm): δ 155.43, 147.78, 136.35. IR (KBr) \tilde{v} : 3459, 3357, 3122, 3029, 2939, 2840, 2777, 2725, 2629, 2575, 2483, 1699, 1641, 1622, 1503, 1450, 1408, 1392, 1187,1086, 1034, 996, 982, 883, 516, 481, 419 cm⁻¹. Elemental analysis (%) for C₃HN₇O₃ (144.08): calculated: C: 19.68, H: 0.55, N: 53.55; found: C: 19.63, H: 0.85, N: 53.89.

2.5.3. N,N'- dinitro-N,N'-bis[5-(tetrazol)furazan-4-yl] methylenediamine (**11**)

The synthesis of compound 11 is similar to compound 3, according to the literature [26]. N,N'-Dinitro-N,N'-bis [3-hydrazino (imino)methyl-furazan-4-yllmethylenediamine (0.386 g, 1 mmol) was added into AcOH (5 ml), the reaction system was cooled to 5 °C, vigorously stirred at this temperature and treated with by dropwise addition of NaNO₂ (0.152 g, 2.2 mmol), and then the reaction mixture was stirred for 1 h at 10-15 °C, acidified with conc. HCl to pH 1, the solvent was removed in vacuo, and the residue was taken up in 10 ml of ethanol, the precipitate that formed was filtered off and recrystallized from ethanol twice. Yield 0.265 g (65%), light grown solid, Dec 148.9 °C. ¹H NMR (DMSO-d₆, ppm): δ6.69 (s, 2H, CH₂ 4.98 (s, 2H, NH); ¹³C NMR (DMSO- d_6 , ppm): δ 151.05, 148.93, ¹⁵N NMR 145.86, 67.61; (DMSO-*d*₆): δ 42.6. 31.9, -33.7, -41.3, -75.8, -206.9 ppm. IR (KBr) v: 3630, 3039, 2924, 2854, 1592, 1407, 1279, 1104, 1021, 996, 897, 751, 733, 647 cm⁻¹. Elemental analysis (%) for C₇H₄N₁₆O₆ (408.05): calculated: C: 20.60, H: 0.99, N: 54.90; found: C: 20.39, H: 0.85, N: 54.71.

2.5.4. N, N'- dinitro-N, N'-bis[5-(tetrazol) furazan-4-yl] ethylenediamine (15)

The synthesis of compound 15 is similar to compound 11. It was recrystallized from MeOH twice. Yield (63%), light grown solid, Dec 163.4 °C. ¹H NMR (DMSO- d_6 , ppm): δ 6.74 (s, 4H, CH₂), 4.74 (s, 2H, NH); ¹³C NMR (d4-MeOH, ppm): δ 152.60, 150.43, 143.75, 51.78; ¹⁵N NMR (d4-MeOH): δ 41.8, 26.9, -32.9, -38.5, -77.2, -214.1 ppm. IR (KBr) \bar{v} : 3636, 3318, 3037, 1625, 1576, 1455, 1348, 1280, 1195, 1044, 1028, 1000, 757, 545 cm⁻¹. Elemental analysis (%) for C₈H₆N₁₆O₆ (422.07): calculated: C: 22.76, H: 1.43, N: 53.08; found: C: 22.63, H: 1.23, N: 53.01. CCDC number: 1567536.

3. Results and discussion

3.1. Synthesis

According to the literature [26,28] and synthesis route depicted in Fig. 2, 4-(1,2,4-oxadiazol-3-yl)furazan-3-amine (1), a luminous yellow solid, was synthesized with high yield and then treated with 80% hydrazine hydrate in methanol at 50 °C for 30 min. Hence, amidrazone of 4-aminofurazan-3-carboxylic acid (2) was obtained as faint yellow solid with high yield. Thereafter compound 2 was treated with AcOH again at 5 °C, and NaNO₂ was slowly added into the reaction mixture at 10–15 °C for 30min, 4-(Tetrazol-5-yl)furazan-3-aminie (3) was obtained as white solid.

Similarly, 3-nitro-4-(1,2,4-oxadiazol-3-yl) furazan (4) was prepared via the method used to synthesize 7. Due to the reducibility of hydrazine and the nitro group of 4 was replaced by hydrazine group, and the oxadiazole ring reacted with hydrazine to change into amidrazone, compound 5 was obtained instead of compound 6. Compound 5 can act as an energetic dication, which would have potential applications in energetic salts. Although compound 5 had been reported by Stepanov [27], its single crystal structure has not been reported. Finally, the ring replaced compound 3-nitro-4-(Tetrazol-5-yl) furazan (7) was finally synthesized via treating compound 3 with classic oxidation mixture of H₂O₂ and concentrated sulphuric acid at 50-55 °C. Compounds 8, 9, 10 and 12, 13, 14 were prepared as described in our previous work. N,N'-dinitro-N,N'-bis [5-(tetrazol)furazan-4-yl] methylene diamine (11) and N,N'dinitro-N,N'-bis [5-(tetrazol)furazan-4-yl] ethylene diamine(15) were obtained as maple solid by successfully employing the same method of synthesis as compound 3;

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Fig. 2. Synthesis route of various compounds.

compound 15 could be recrystallized from the mixture of methanol and water as white diamond crystals.

3.2. Spectroscopy and X-ray crystallography

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The novel 15 was characterized by 1H and ¹³C NMR spectra; the compounds 11 and 15 were further characterized using ¹⁵N NMR spectra (Fig. 3, and Figs. S10–S12). The protons of compound 5 were consistent with compound 2 and other reported data in the literature. The signals in the ¹H NMR spectra of tetrazole protons and

methylene protons in compound 11 were 6.69 and 4.98 ppm, respectively, which are also similar to the reported data [33]. For compound 15, the signals of ¹H NMR spectra were 6.74 and 4.74 ppm, which correspond to the tetrazole protons and ethylene protons, respectively. The ¹H NMR signals of ethylene group of 15 were slightly upshifted compared to methylene group of compound11 which is because the ethylene group can provide more electrons than methylene group. The ¹³C NMR signals of tetrazole rings and furazan ring are similar (δ = 151.05, 148.93, and 145.86 for compound 11; δ = 152.60, 150.43, and 143.75 for compound 15) for



both the compounds 11 and 15. The signal of ¹³C NMR for the methylene group of compound 11 was 67.29, which is different from that of compound 15 ($\delta = 51.78$), this is because the solubility of compound 15 is poor in DMSO- d_6 , the ¹³C signals of compound 15 were obtained in *d*4-MeOH. The ¹⁵N NMR spectra of compounds 11 and 15 are also similar, only the position of N5 was slightly different, this is because the ethylene group can provide more electrons than methylene group.

The light brown needle crystals of compound 5 were slowly recrystallized from water. The compound 5 crystallized with monoclinic (P 121/c1) symmetry with eight molecules in each lattice cell (Z = 8) and the density of 1.603 g cm⁻³ at 296 K. The atoms which from furazan ring, amino group, and hydrazine group are nearly coplanar accompanying torsions (N7–N6–C1–C2:4.79°; N5–N4–C3–C2:3.64°; N5–N4–C3–N3:3.73°) close to zero. An intramolecular hydrogen bond formed between hydrogen atoms connecting N6 and N4, which is repeated throughout the crystal. (Fig. 4a and b, and Figs. S6–S7).

The white block crystal 15 recrystallized slowly from the mixture of H₂O and methanol with triclinic (P -1) symmetry having one compound 15 molecule and two methanol molecules in each lattice cell (Z = 1) (Fig. 4c and d, and Figs. S8–S9) and the density of 1.62 g cm⁻³ at 296 K. It was put in infrared oven for 24 h, in order to remove the methanol molecular exited in compounds completely, and then its measured is 1.77 g cm⁻³ at room temperature by gas pycnometer. The crystal structure of 15 was symmetrical with two 3-nitramino-furazantetrazole anions bridged by ethyl group. The furazan ring and the tetrazole ring for both sides of

ethyl group are nearly coplanar (torsion of N1–C1–C2–N5: 9.19°) and the torsion (C2–C3–N7–N8) between nitramino and furazan ring was 63.69°. There are two kinds of hydrogen bonds extensively throughout the crystal. The first hydrogen bond of N-H…O with bond length 1.717 Å where the hydrogen atom is from the tetrazole ring while the oxygen atom is from molecular methanol. The second hydrogen bond O–H…N of bond length 2.012 Å where the hydrogen atom is from the methanol while the nitrogen atom is from the tetrazole ring. As to crystal 13, it crystallized with monoclinic (P21/n) symmetry with two molecules in each lattice cell (Z = 2) and a density of $1.750 \,\mathrm{g \, cm^{-3}}$ at 150 K, its density in room temperature is 1.68 g cm^{-3} . The atoms in the furazan core and 1,2,4-oxadiazole are nearly coplanar with a torsion angle close to zero. The nitramine moieties in this crystal are also considerably twisted to the furazan and 1,2,4-oxadiazole plane with torsion angles 118.41°. After calculation of packing coefficient by MolInfo, the packing coefficients of compounds 13 and 15 are 55.45% and 74.32%, respectively. It is clear that the packing mode of 15 is closer than that of 13, which lead to a higher density of 15.

3.3. Physicochemical and energetic properties

Thermal stability is one of the most vital physicochemical parameters of energetic compounds; hence, all the newly synthesized compounds were measured at $5 \,^{\circ}$ C min⁻¹ in the nitrogen environment (Table 1). The decomposition temperatures of compound 5 and 7 were 198.8 $^{\circ}$ C and 215 $^{\circ}$ C, respectively. Also, the decomposition temperatures of compounds 11 and 15 were 149 and



Fig. 4. (a): Single-crystal X-ray structure of compound 5; (b): the package structure of compound 5 from the view of b-axis; (c): Single-crystal X-ray structure of compound 15; (d): the package structure of compound 15 from the view of b-axis.

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Table 1

Physicochemical and detonation parameters of the synthesized compounds.

Compound	$T_m^a (^\circ C)$	T_d^b (°C)	N ^c (%)	d ^d (g cm ⁻³)	$\Delta_{\rm f} H^{\rm e}[kJ\ mol^{-1}\ (kJ\ g^{-1})]$	$v_D^{f}(m \ s^{-1})$	P ^g (GPa)	IS ^h (J)	FS ⁱ (N)
2		169.4	58.31	1.60	246.4/1.71	8201	22.63	>40	>360
4	55		38.3	_	327.1/1,79				
5		198.8	62.4	1.60	352/2.24	8090	22.44	>40	>360
7	120	215	53.6	1.75	486/2.91	8585	30.55	6	112
9	124	149	41.2	1.77	586.2/1.44	8182	27.70	27	240
10	115	138	50.8	1.64	810.7/2.10	8126	25.3	>40	>360
11	96	149	54.9	1.82	1249.4/3.06	8874	33.86	11	96
13	142	175	39.8	1.75	785.8/1.88	8185	27.9	31	240
14	128	145	49.0	1.60	797.6/1.99	7914	23.3	>40	>360
15	97	163	53.1	1.77	1239.8/2.94	8589	30.51	17	144
TNT ^j	81	295	18.5	1.65	55.7/0.25	7459	23.5	15	353
PETN ^j	141	160	32.6	1.77	-502.8/-1.59	8564	31.3	3	60
RDX		205	37.8	1.81	79.2/0.36	8748	34.9	7	120

^a Melting temperature.

^b Thermal decomposition temperature (onset) under nitrogen gas (DSC, 5 °C min⁻¹).

c Nitrogen content.

^d Density measured by gas pycnometer (25 °C).

e Calculated heat of formation.

^f Detonation velocity.

^g Detonation pressure.

^h Impact sensitivity.

ⁱ Friction sensitivity.

^j Ref [30-32].

163 °C (Figs. S1–S5), respectively, which are similar to their precursors.

The enthalpies of formation of all the resultant compounds were calculated using isodesmic equations and G03 software program [29] (see Electronic Supplementary Information). Compound 4 has the enthalpy of formation of 327.1 kJ mol⁻¹/1.79 kJ g⁻¹. As the oxadiazole ring was replaced by tetrazole ring, the enthalpy of formation of compound 7 improved significantly up to 486 kJ mol⁻¹/2.91 kJ g⁻¹. In the case of compounds 11 and 15, owing to a high enthalpy of formation of tetrazole, their enthalpies of formation reached up to 1249.4 kJ mol⁻¹/3.06 kJ g⁻¹ and 1239.8 kJ mol⁻¹/2.94 kJ g⁻¹, respectively. Additionally, their nitrogen contents were improved to 54.90 and 53.08%, respectively, which are clearly higher than their precursors and place them in the category of high nitrogen content energetic materials.

With the measured densities and calculated enthalpies of formation in hand, the detonation properties of the synthesized compounds were determined by EXPLO5 v6.01 version. We can observe from Table 1 that the detonation velocity and pressure of compound 7 were estimated to be 8585 m s^{-1} and 30.55 GPa, respectively. A relatively simple synthesis route and excellent performance make it comparable to PETN. Compound 5 can act as a potential dication of energetic salt, although its density of $1.60 \,\mathrm{g}\,\mathrm{cm}^{-3}$ is lower than that of TNT, because of its higher heat of formation, which also leads to markedly better detonation properties than TNT [30-32]. In the case of compounds 11 and 15, owing to the higher heats of formation brought by tetrazole ring as compared to their precursors, the detonation velocities and pressure increased remarkably relative to those of compounds 9,10 and 13,14, reaching to 8874, 8589 m s⁻¹ and 33.86, 30.51 GPa, respectively, and showing comprehensive comparative to the detonation properties of RDX and PETN, respectively. Hence, this ring replacement strategy has opened novel avenues to improve properties of energetic compounds.

4. Conclusions

In this work, we employed ring replacement strategy to replace the oxadiazole rings of the original compounds with tetrazole rings. Due to the high heat of formation and high nitrogen content of tetrazole ring, the enthalpies of formation of the ring-replaced compounds 11 and 15 were improved to $3.06 \text{ kJ} \text{ mol}^{-1}$ and $2.94 \text{ kJ} \text{ mol}^{-1}$, respectively, while the nitrogen content of these two compounds reached up to 54.90% and 53.08%, respectively. The detonation properties of the resultant two compounds were improved to 8874, 8589 m s^{-1} and 33.86, 30.51 GPa, respectively, showing comprehensive compared to the detonation properties of RDX and PETN, and are higher than those of original compounds. 3-nitro-4-tetrazolefurazan (7) has excellent energetic performance relative to PETN and may act as a potential replacement for PETN. To summarize, the ring replacement strategy was designed and implemented successfully and offers fresh routes for the improvement in properties of energetic materials.

Author contributions

Jichuan Zhang and Guangxing Pan contribute equally to this work, they performed the NMR, physicochemical and energetic properties experiments. Jichuan Zhang, Jiaheng Zhang and Guangxing Pan wrote the paper. Jun Yang, Jiaheng Zhang and Haifeng Huang performed the theoretical calculations. Jiaheng Zhang and Jun Yang conceived and designed the project.

Declaration of competing interest

The authors declare no competing interests.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molstruc.2019.127358.

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