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## Computational study on pure N<sub>8</sub> as high energy density materials

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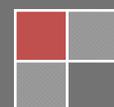
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### ABSTRACT

Six novel N<sub>8</sub> structures are devised and fully optimized by high-precision quantum chemical calculations. Their thermal stabilities are analyzed in terms of molecular electronic structures, the Wiberg bond index, frontier orbital energies, heat of formation and molecular electrostatic potential. The results show that the fused aromatic ring structure is more stable than cage structure. Compared to RDX and HMX explosives, six N<sub>8</sub> isomers are better to be good potential high energy density materials.

### KEYWORDS

High energy density materials; Thermal stability; Wiberg bond index; Heat of formation; Molecular electrostatic potential.



## INTRODUCTION

As good candidates for high energy density materials (HEDM), nitrogen clusters have been attracted lots of attentions in respect of the relationship between the relative stability of materials and detonation performances. It is attributed that the enormous energy difference between the single and double bonds in the nitrogen clusters and the triple bond in the sole explosive product  $N_2$ . Lots of studies on nitrogen clusters for a number of years both theoretically and experimentally have shown there are stable structures in  $N_x$  ( $x > 2$ ) clusters<sup>[1-11]</sup>. In 20<sup>th</sup> century, it is true that we only know the pure nitrogen materials were  $N_2$  and  $N_3^-$ . In 1999, Christe et al. first synthesized the  $N_5^+AsF_6^-$  salt by reacting  $N_2F^+AsF_6^-$  with  $HN_3$  in anhydrous fluoride at  $-78^\circ C$ . Later they reported that the  $(N_5^+Sb_2F_{11}^-)$  and  $(N_5^+SbF_6^-)$  salt were stable up to  $70^\circ C$ , and identified the  $N_5^-$  in the gas phase<sup>[2-5]</sup>.

Duo to the successful experimental synthesis of  $N_5^+$ , it is expected that the combination of three-atom azide anion  $N_3^-$  with  $N_5^+$  cation to create  $N_8$ . Owing to the difficulties in the synthesis of  $N_8$ , the theoretical calculation could be considered as a relatively effective way to design and predict its isomer structures and properties to give some useful guides for experiment. Some structures of  $N_8$  isomers have been already predicted theoretically<sup>[7-8]</sup>. In 2012, Hirshberg and Gerber studied the decomposition mechanisms and dynamics of  $N_6$ <sup>[10]</sup>. More recently, polymeric form  $N_8$  has been predicted to exist and stabilize as a chain up to room temperature in confinement of nanostructures<sup>[11]</sup>. Here we study the thermal stabilities of six novel  $N_8$  isomers according to the molecular electronic structures, the Wiberg bond index, heat of formation and molecular electrostatic potential (MESP), respectively.

## COMPUTATIONAL METHODS

All calculations were performed with Gaussian 09 suite of programs<sup>[12]</sup>. The geometries of six isomers were optimized by B3LYP, MP2 and CCSD method with 6-31G\* basis set, respectively. The Wiberg bond index<sup>[13]</sup> was analyzed at B3LYP/6-311++G\*\* level. The standard gaseous heat of formation was calculated by the atomic scheme with the formulas following<sup>[14]</sup>:

$$\square_f H^0(M, 0K) = \sum_{atoms} x \square_f H^0(X, 0K) - \left[ \sum_{atoms} x \varepsilon_0(X) - \varepsilon_0(M) - \varepsilon_{ZPE}(M) \right] (1)$$

$$\square_f H^0(M, 298.15K) = \square_f H^0(M, 0K) + (H_M^0(298.15K) - H_M^0(0K)) - \sum_{atoms} x (H_X^0(298.15K) - H_X^0(0K)) (2)$$

Where M stands for molecule, X represents element making up M, and x denotes the number of atoms of X in M.  $\varepsilon_0(M)$  and  $\varepsilon_{ZPE}(M)$  are the total energy and zero point energy of molecule M, respectively.  $\square_f H^0(M, 0K)$  and  $\square_f H^0(M, 298.15K)$  stand for heat of formation of molecule M at 0 K and 298 K, respectively<sup>[15]</sup>.

## RESULTS AND DISCUSSION

All the optimized stable molecules are characterized as the energy minima of the potential surfaces by frequency identification according to three different methods. The optimized structures of six  $N_8$  isomers calculated at B3LYP/ 6-31G\* level are presented in Figure 1, and their corresponding geometrical parameters are listed in TABLE S1 (available in Electronic Supplementary Information, ESI). The experimental length of N–N is 1.449 Å ( $NH_2-NH_2$ ) and N=N is 1.252 Å ( $N_2H_2$ ). Whereas the so-called aromatic bond length is between single bond and double bond, and the  $\pi$  electrons are delocalized<sup>[16]</sup>. The Wiberg bond indexes of six  $N_8$  isomers are listed in Table S2 (available in ESI). The Wiberg bond index values of N–N and N=N should be equal to 1 and 2, respectively. Structure 1 is a planar cyclic structure with  $D_{2h}$  symmetry. The Wiberg bond index analysis shows that the value of N4-

N7 (1.8733) is equal to N5-N6 close to double bond order. Structure 3 is a chair-shaped cyclic structure with C<sub>2h</sub> symmetry. The Wiberg bond index indicates all the bonds are the typical single-bonds. Structure 2 (C<sub>2v</sub>), structure 5 (C<sub>2v</sub>) and structure 6 (C<sub>3</sub>) are different cage structures. The Wiberg bond index values are all close to 1. For structure 4, the Wiberg bond index analysis shows that there are the powerful  $\pi$  conjugation between N5-N7 bond and N6-N7 bond. In summary, it is clear that the trend of bond lengths is consistent with that of Wiberg bond indexes.

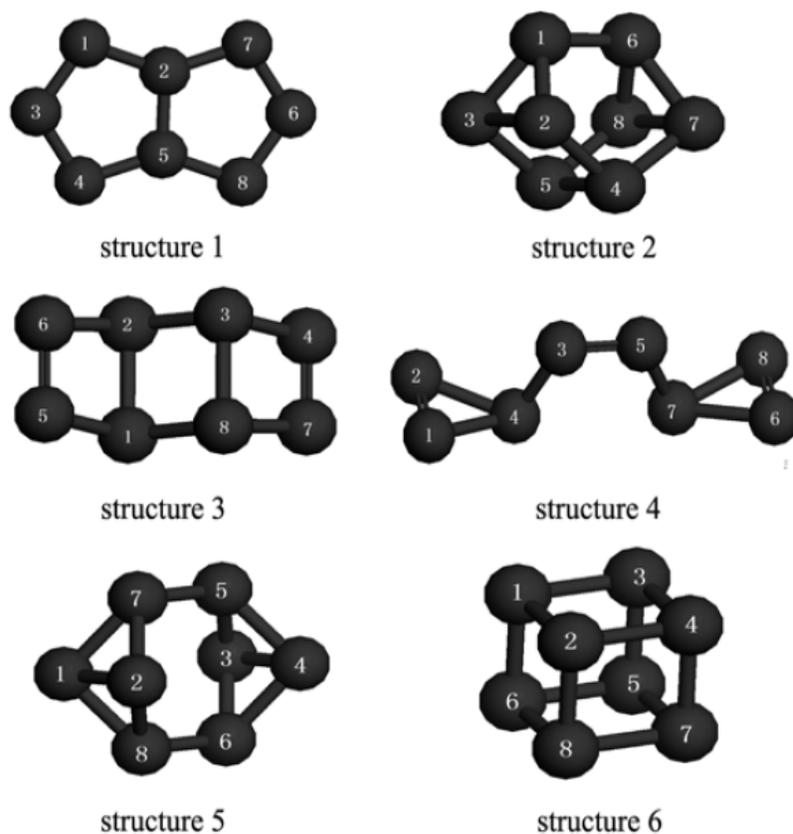


Figure 1: The optimized molecular structures of six N<sub>8</sub> isomers

The molecular frontier orbital energies and gaps of six N<sub>8</sub> isomers at B3LYP/ 6-311++G\*\* level are listed in TABLE 1. The energy gaps are in the order 1>2>5>6>3>4. The values refer to the molecular stability in the photochemical or chemical processes with electron leap or electron transfer.

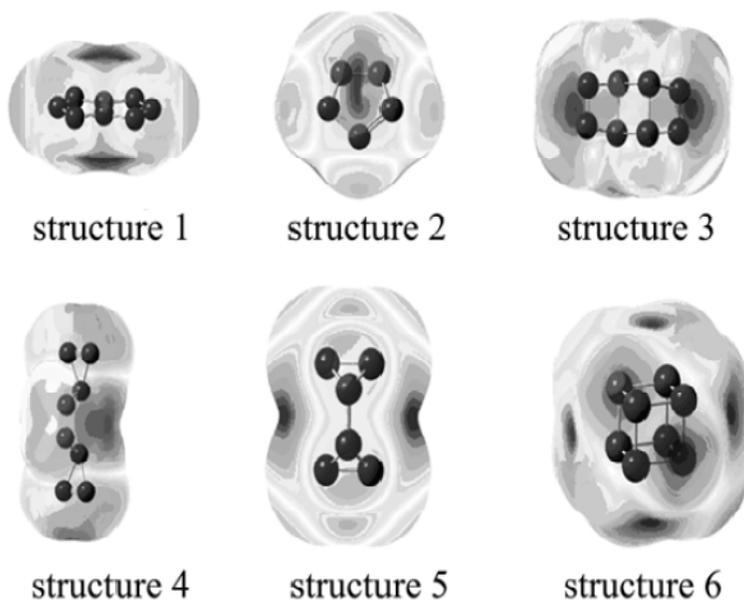
TABLE 1: Energies of highest occupied molecular orbital ( $E_{\text{HOMO}}$ ) and lowest unoccupied molecular orbital ( $E_{\text{LUMO}}$ ), and energy gaps  $\epsilon$  ( $\Delta E_{\text{LUMO-HOMO}}$ ) for N<sub>8</sub> isomers. (kJ/mol)

Molecule	1	2	3	4	5	6
$E_{\text{HOMO}}$	-877.4684	-868.5417	-846.4875	-760.3711	-832.8611	-816.7931
$E_{\text{LUMO}}$	-274.9424	-288.6737	-379.1747	-339.3459	-306.2908	-327.9512
$\epsilon$	602.5523	579.9730	467.3390	421.1302	526.6753	488.8681

The results of heat of formation for N<sub>8</sub> isomers are listed in TABLE 2. It is one of the most significant physical quantities to judge the explosive performance for the energetic compounds. The heat of formation is calculated at B3LYP/6-31G\* level, and the absolute values decrease in the order 1>4>3>2>5>6.

**TABLE 2: Calculated molecular total energy ( $E_0$ ), Zero point energy (ZPE) and thermal correction ( $H_T$ ) and gas-phase heat of formation (HOF) at 0 and 298 K. (kJ/mol)**

Molecule	1	2	3	4	5	6
$E_0 (\times 10^6)$	-1.1494	-1.1488	-1.1489	-1.1491	-1.1486	-1.1485
ZPE	99.0129	86.5811	89.7895	74.5196	79.0801	90.0153
$H_T$	111.1978	100.9925	105.9494	97.0437	95.6548	103.7178
HOF (0K)	-1239.4315	-630.4599	-781.2634	-945.4937	-524.0012	-334.4611
HOF (298K)	-1262.0574	-650.8595	-799.9143	-957.7804	-542.2373	-355.5695

**Figure 2: Molecular electrostatic potentials of six  $N_8$  isomers**

Contour plots of molecular electrostatic potential are displayed in Figure 2 (The corresponding colour one Figure S1 is available in ESI). It gives a visual way to comprehend the electronic distribution of the molecules. MESP values are mapped on the electron density surface for a simple comparison, from red to blue denoting MESP from negative to positive. In the structures 1, 3 and 4, their highest negative values of the electrostatic potential are all located at the  $\pi$  conjugation. In the structures 2, 5 and 6, the charge distribution is relatively dispersed.

## CONCLUSIONS

In this manuscript, six novel  $N_8$  isomers are investigated by high-precision quantum chemical calculations. The results show that they have good thermodynamic properties to be considered as the potential HEDM candidates. The subsequent calculations of the explosive and decomposition properties are in progress.

## ACKNOWLEDGMENTS

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## SUPPLEMENTARY INFORMATION

Supplementary Information related to this article presents the optimized geometrical parameters and the Wiberg bond indexes of six N<sub>8</sub> isomers (Table S1 and S2), as well as the colour contour plots of molecular electrostatic potentials of six N<sub>8</sub> isomers (Figure S1).

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