

# Comparative theoretical investigation of the structures, energetics, and stabilities of $C_7N_5H_{11}$ cages

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**Abstract** Carbon-nitrogen cages are the focus of much research due to their potential use as high energy density materials (HEDMs). Several such cage isomers of  $C_7N_5H_{11}$ , created by modifying the most stable  $N_{12}$  cage, were examined by performing theoretical calculations to evaluate their suitability as potential HEDMs. Calculations were carried out with density functional theory and Møller–Plesset perturbation theory (MP2) using the basis sets 6-31+G(d,p) and cc-pvdz. The relative thermodynamic stabilities of the isomers were explored in two ways: (1) the thermodynamic stability of one isomer was compared to that of another isomer based on their relative energies; (2) the kinetic stabilities of the isomers were determined by calculating the corresponding bond-breaking energies.

**Keywords** Density functional theory · Second-order perturbation theory · Stability

## Introduction

Molecules consisting entirely of nitrogen atoms have been extensively studied as candidates for high energy density materials (HEDMs) [1, 2]. Pure nitrogen molecules such as  $N_4$ ,

$N_5$ ,  $N_6$ ,  $N_7$ ,  $N_8$ ,  $N_{10}$ ,  $N_{12}$ ,  $N_{18}$ ,  $N_{20}$ ,  $N_{24}$ ,  $N_{30}$ , and  $N_{36}$  have been studied theoretically [2–21]. Such a pure nitrogen molecule  $N_x$  can decompose into  $N_2$  in a highly exothermic ( $\geq 50$  kcal mol<sup>-1</sup> per nitrogen atom) and environmentally friendly process.

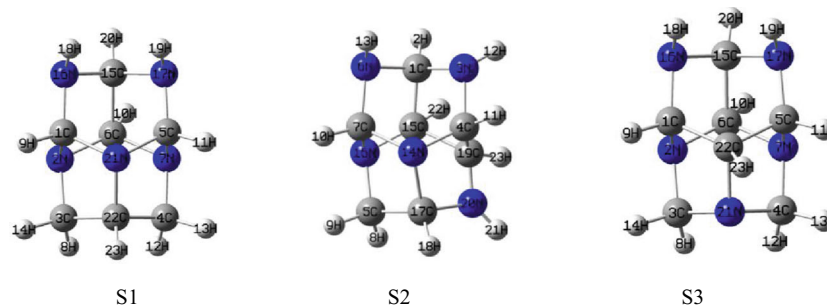
However, although it is possible to identify which of the nitrogen cages are the most stable, it has been shown that even the most stable  $N_{12}$  cage is unstable with respect to dissociation [22, 23]. Thus, attempts have been made to substitute some of the nitrogen atoms in  $N_x$  cages with carbon (or boron) to form C–N cages, which are potentially stable HEDMs due to their high heats of formation (HOFs) and compact structures [24]. Thus, in the work reported in the present paper, we designed three  $C_7N_5H_{11}$  cage molecules that could be candidates for HEDMs if they can be synthesized. We explored the optimized structures, heats of formation (HOFs), densities, detonation energies, and stabilities of these molecules to determine whether they are potentially novel high-energy explosives.

## Computational methods

Density functional theory (DFT) has emerged as an effective theoretical method of optimizing the geometries of energetic compounds [25–27]. However, the application of the MP2 method along with a high-quality basis set gives more reliable results when investigating complexation energies [28–30]. Thus, the DFT-B3LYP and MP2 methods were used in this work, in combination with the 6-311+G(d,p) and cc-pVTZ basis sets. All of the structures described later in the paper were obtained through optimization to local minima. The Gaussian 03 program was used for all calculations [31].

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**Fig. 1** Optimized structures of the three C<sub>7</sub>N<sub>5</sub>H<sub>11</sub> isomers

The empirical Kamlet–Jacobs equations [32], which are widely employed to estimate the detonation velocities and detonation pressures of energetic materials, were used:

$$D = 1.01 \left( N \bar{M}^{1/2} Q^{1/2} \right)^{1/2} (1 + 1.30\rho) \quad (1)$$

$$P = 1.558 \rho^2 N \bar{M}^{1/2} Q^{1/2}, \quad (2)$$

where  $D$  is the detonation velocity (km s<sup>-1</sup>),  $P$  is the detonation pressure (GPa),  $\rho$  is the density of the explosive (g cm<sup>-3</sup>),  $N$  is the number of moles of gaseous detonation products per gram of explosives,  $\bar{M}$  is the average molecular weight of the

**Table 1** Bond lengths (Å) and bond angles (°) of the three C<sub>7</sub>N<sub>5</sub>H<sub>11</sub> isomers

S1		S2		S3			
Bond length/angle	Value	Bond length/angle	Value	Bond length/angle	Value		
C3–C22	1.552	C1–C15	1.607	C4–C20	1.529	C5–C22	1.599
C4–C22	1.552	C5–C17	1.544	C15–C20	1.580	C6–C15	1.593
C6–C15	1.599	C1–N3	1.474	C1–N6	1.466	C1–N2	1.470
C1–N2	1.463	C4–N3	1.461	C4–N14	1.516	C1–N16	1.451
C1–N16	1.438	C7–N6	1.435	C7–N14	1.549	C3–N2	1.458
C1–N21	1.544	C7–N16	1.462	C15–N16	1.512	C3–N21	1.490
C3–N2	1.464	C17–N14	1.542	C20–N21	1.447	C6–N2	1.514
C6–N2	1.513					C6–N7	1.513
C15–N16	1.469					C15–N16	1.469
C22–N21	1.524						
N2–C1–N21	103.4	N4–C3–N6	104.0	N3–C1–C15	107.9	N2–C1–C22	99.6
N16–C1–N21	101.2	N6–C1–C15	103.3	C1–N3–C4	100.7	N16–C1–C22	118.8
C1–N2–C6	97.9	N3–C4–N14	114.5	N3–C4–C20	105.7	N2–C1–N16	100.6
C1–N2–C3	99.7	N14–C4–C20	99.3	C1–N6–C7	100.2	C1–N2–C3	99.7
C3–N2–C6	115.0	N16–C5–C17	102.1	N6–C7–N14	117.2	C3–N2–C6	113.7
N2–C3–C22	101.7	N14–C7–N16	103.7	C4–N14–C7	109.6	C1–N2–C6	98.9
N2–C6–N7	116.3	C4–N14–C17	102.4	C7–N14–C17	101.4	N2–C3–N21	105.8
C6–C15–N16	103.1	C1–C15–N16	101.8	C1–C15–C20	101.6	N2–C6–N7	115.9
C1–N16–C15	100.7	N16–C15–C20	113.3	C5–N16–C7	99.9	N2–C6–C15	102.1
C1–N21–C5	107.9	C5–N16–C15	114.5	C7–N16–C15	97.9	C6–C15–N16	103.2
C1–N21–C22	101.6	C5–C17–N14	104.7	C5–C17–N21	102.3	N16–C15–N17	110.9
C4–C22–N21	105.0	N14–C17–N21	109.0			C1–N16–C15	101.4
C3–C22–C4	102.0					C3–N21–C4	102.3
						C3–N21–C22	103.0
						C1–C22–N21	103.5
						C1–C22–C5	107.4

**Table 2** Selected properties of the three C<sub>7</sub>N<sub>5</sub>H<sub>11</sub> isomers

Isomer	Symmetry	$E_H$ (eV)	$E_L$ (eV)	$\Delta E_{L-H}$ (eV)	$E_0$ (a.u.)	FIE (eV) <sup>a</sup>
S1	C <sub>1</sub>	-0.21145	0.06835	0.27980	-547.02603	0.21145
S2	C <sub>1</sub>	-0.20534	0.06619	0.27153	-547.02910	0.20534
S3	C <sub>1</sub>	-0.21610	0.06309	0.27919	-547.02443	0.21610

<sup>a</sup> First ionization energy

detonation products, and  $Q$  is the detonation energy (cal g<sup>-1</sup>).  $N$ ,  $\bar{M}$ , and  $Q$  were determined via the most exothermic principle.

The thermodynamic stability of a molecule can be evaluated using the bond dissociation energy (BDE) [33–35], which is calculated as follows:



$$BDE(A - B) = [HOF(A \cdot) + HOF(B \cdot)] - HOF(A - B) \quad (4)$$

Here, A—B represents the neutral molecule and A· and B· are the corresponding radical products produced by breaking the A—B bond. BDE(A—B) is the bond dissociation energy of the bond A—B. HOF is the standard heat of formation, so HOF(A·), HOF(B·), and HOF(A—B) are the standard heats of formation of the products and the neutral molecule (the reactant) at 298 K, respectively.

However, in the present work, the BDE is defined as the difference between the total energy of the products of unimolecular bond dissociation at 0 K and the energy of the reactant in this process. Therefore, we computed the

BDE at 0 K according to the energy changes involved in the bond-breaking process as follows:

$$BDE(A - B) = \Delta E = [E(A \cdot) + E(B \cdot)] - E(A - B). \quad (5)$$

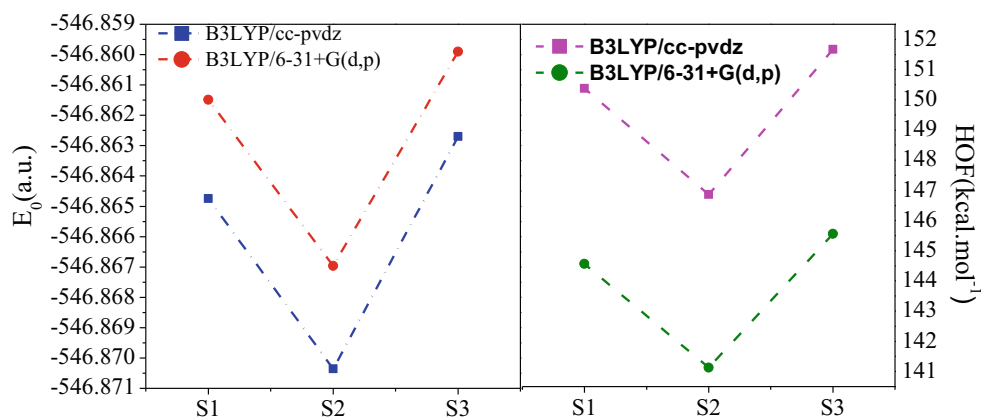
## Results and discussion

### Molecular structures and electronic properties

Figure 1 shows the geometries of the three isomers optimized at the B3LYP/6-31G (d) level. Table 1 lists the representative parameters.

It can be seen that almost all C—C bonds of the three isomers are longer than a “normal” C—C bond (1.540 Å), except for C4—C20 (1.529 Å) in isomer 2. The longest C—C bond is 1.607 Å. If we consider the C—C bonds between the six-membered rings in isomers 1, 2, and 3, C3—C22 (1.552 Å), C15—C20 (1.580 Å), and C6—C15 (1.593 Å) are all shorter than C6—C15 (1.599 Å), C1—C15 (1.607 Å), and C5—C22 (1.599 Å) in the pentagon.

Through careful analysis of these different C—C bonds, it was found that the longest C—C bond is that between the hexagons and the pentagons, i.e., C6—C15 (1.599 Å) for isomer 1 and C1—C15 (1.607 Å) for isomer 2. In isomer 3, there is no C—C bond at the junction between the pentagons and hexagons. Meanwhile, most of the C—N bond lengths are

**Fig. 2** Correlation between structure and energy

**Table 3** Total energies  $E_0$  (a.u.) and HOFs (kcal mol<sup>-1</sup>) for reference compounds and the three isomers

Parameter	Level of theory	Compound/species/isomer					
		H <sub>2</sub>	C(s)	N <sub>2</sub>	S1	S2	S3
$E_0$	B3LYP/6-31+G(d,p)	-1.16838	-37.85134	-109.52978	-546.86475	-546.87036	-546.86270
	B3LYP/cc-pvdz	-1.16365	-37.85198	-109.53338	-546.86149	-546.86696	-546.85990
HOF	B3LYP/6-31+G(d,p)	0	0	0	150.38	146.86	151.67
	B3LYP/cc-pvdz	0	0	0	144.56	141.13	145.56

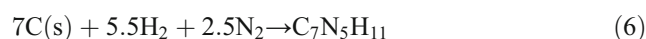
within the normal range (1.470 Å), and the longest C–N bond is C1–N21 (1.544 Å), located at the junction of the pentagons and hexagons. The smallest bond angles in isomer 1, isomer 2, and isomer 3 are 97.9, 97.9, and 99.6°, respectively, which are larger than the ~90° seen in cubane (C<sub>8</sub>H<sub>8</sub>). Thus, we can conclude that these structures are subject to a certain degree of ring strain, but are weaker than those in cubane and may release additional energy upon detonation.

Some properties of the investigated molecules have been tabulated in Table 2. The total energy ( $E_0$ ) of the isomer increases in the order S2<S1<S3. The largest energy gap  $\Delta E_{L-H}$  between the highest occupied molecular orbital  $E_H$  and the lowest unoccupied molecular orbital  $E_L$  is 0.27980 eV, for isomer 1, indicating that this isomer is the most stable one. Here, we are referring to stability with respect to a chemical or photochemical process involving an electron transfer or leap, with such a process being initiated from an excited state.

It is worth noting that the calculated first ionization potentials are 0.21145 eV for isomer 1, 0.20534 eV for isomer 2, and 0.21610 eV for isomer 3, respectively. Isomer 3 has the highest first ionization potential, indicating that it is more difficult to remove an electron from this isomer than from the other two isomers. It is reasonable to assume that the structural parameters and electronic properties listed in Tables 1 and 2 are accurate and could be utilized by experimentalists to determine the structures of these compounds, should they be synthesized.

### Heat of formation

A key property of an energetic material that is used to assess its potential performance in a gun or warhead is its heat of formation (HOF), as this parameter enters into calculations of explosive and propellant properties such as the detonation velocity, detonation pressure, and detonation energy. DFT methods have proven accurate for computing HOFs via appropriate reactions [36–48]. In the present work, the HOFs of the title compounds were calculated with the help of the following reaction:



Given the calculated enthalpies of all species and the experimental sublimation enthalpy of graphite, it is easy to obtain the HOFs of the title compounds.

It can be seen that the difference between the results calculated using the two basis sets is around 5 kcal mol<sup>-1</sup> (see Fig. 2 and Table 3). The HOFs of the title compounds are all positive, and the largest, 151.67 kcal mol<sup>-1</sup> for S3, is close to the HOF (691.30 kJ mol<sup>-1</sup>) of hexanitrohexaazaisowurtzitane (CL-20) [46]. A large HOF is a prerequisite for an energetic material as it increases the heat released during detonation.

**Table 4** Densities (g cm<sup>-3</sup>) and detonation energies (kJ g<sup>-1</sup>) of the three C<sub>7</sub>N<sub>5</sub>H<sub>11</sub> cages studied in the present work

Parameter	Level of theory	Isomer		
		S1	S2	S3
$\rho$	B3LYP/6-31+G(d,p)	1.464	1.479	1.487
	B3LYP/cc-pvdz	1.488	1.513	1.484
	mp2/6-31+G(d,p)	1.480	1.492	1.481
	mp2/cc-pvdz	1.480	1.484	1.470
$\Delta H_C$	B3LYP/6-31+G(d,p)	-27.55	-27.47	-27.59
	B3LYP/cc-pvdz	-27.61	-27.52	-27.63
	mp2/6-31+G(d,p)	-26.20	-26.15	-26.22
	mp2/cc-pvdz	-26.48	-26.39	-26.50

**Table 5** Bond properties and relative energies (kcal mol<sup>-1</sup>) of the three isomers

		Isomer		
		S1	S2	S3
Bond	C–C	3	4	3
	C–N	13	12	13
Energy	B3LYP/6-31+G(d,p)	-1.12	-4.78	0
	B3LYP/cc-pvdz	-0.79	-4.38	0
	mp2/6-31+G(d,p)	-0.94	-4.71	0
	mp2/cc-pvdz	-0.74	-4.34	0

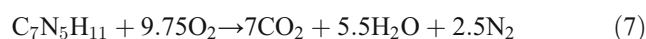
### Density and combustion energy

Density ( $\rho$ ) is an important factor that is helpful when evaluating an explosive performance, as this parameter ultimately decides which molecule releases the most energy upon combustion, given that the main source of this energy is the velocity of detonation of the molecule, which is a function of its density.

Studies have indicated that when the average molar volume estimated via a Monte Carlo method based on an isosurface of electron density of 0.001 electrons/bohr<sup>3</sup> is used, the theoretical molecular density is very close to the experimental one [43–48]. It is worth noting that the average volume used here should be the statistical average of at least 100 volume calculations divided by the molar mass.

The amount of energy released during combustion  $\Delta H_C$  is another important parameter that reflects the explosive performance of an energetic material. The following reaction was

used in this work to calculate the  $\Delta H_C$  values of the title compounds:



It is known that the more energy a compound releases on combustion, the greater the energy stored by the molecule, and the more sensitive its structure. It is evident from Table 4 that isomer 2 is the most stable, which means that its detonation energy is the lowest of the isomers. The detonation energies for all three isomers are negative, indicating that these reactions are exothermic, and the maximum heat released on the combustion of an isomer is -27.63 kJ g<sup>-1</sup> (for isomer 3), which is much larger than the maximum heat released on the combustion of CL-20 (-6.03 kJ g<sup>-1</sup>) [46] or ONC (-7.49 kJ g<sup>-1</sup>) [49]. Therefore, this series of cage compounds appear to be good candidates for potential high energy density materials.

**Table 6** Bond-breaking energies (kcal mol<sup>-1</sup>) for C<sub>7</sub>N<sub>5</sub>H<sub>11</sub> isomers, calculated using the cc-pvdz basis set

Bond	S1		Bond	S2		Bond	S3	
	B3LYP/cc-pvdz	MP2/cc-pvdz		B3LYP/cc-pvdz	MP2/cc-pvdz		B3LYP/cc-pvdz	MP2/cc-pvdz
C3–C22	84.02	75.56	C1–C15	61.65	78.38	C1–C22	71.68	67.93
C4–C22	84.02	75.56	C4–C20	71.90	64.47	C5–C22	71.68	67.93
C6–C15	81.86	74.22	C5–C17	84.73	75.37	C6–C15	81.83	73.59
C1–N2	67.45	64.04	C15–C20	47.39	67.49	C1–N2	67.94	64.03
C1–N16	93.34	85.08	C1–N3	87.07	77.61	C1–N16	94.46	85.56
C1–N21	60.22	59.26	C1–N6	88.77	78.45	C3–N2	75.06	70.40
C3–N2	79.46	72.91	C4–N3	87.88	78.65	C3–N21	74.66	69.28
C4–N7	79.46	72.91	C4–N14	60.70	59.71	C4–N7	75.06	70.40
C5–N7	67.45	64.04	C5–N16	84.49	75.57	C4–N21	74.66	69.28
C5–N21	60.22	59.26	C7–N6	95.58	84.89	C5–N7	67.94	64.03
C6–N2	64.08	63.12	C7–N14	64.08	61.41	C5–N17	109.97	94.84
C6–N7	64.08	63.12	C15–N16	71.62	68.76	C6–N2	66.71	65.99
C15–N16	87.87	79.31	C17–N14	69.82	68.00	C6–N7	66.71	65.99
C15–N17	87.87	79.31	C17–N21	92.71	83.75	C15–N16	67.63	80.25
						C15–N17	67.63	80.25

**Table 7** Bond-breaking energies (kcal mol<sup>-1</sup>) for C<sub>7</sub>N<sub>5</sub>H<sub>11</sub> isomers, calculated using the 6-31+(d, p) basis set

Bond	S1		Bond	S2		Bond	S3	
	B3LYP/ 6-31+G(d, p)	MP2/ 6-31+G(d, p)		B3LYP/ 6-31+G(d, p)	MP2/ 6-31+G(d, p)		B3LYP/ 6-31+G(d, p)	MP2/ 6-31+G(d, p)
C3–C22	86.70	74.03	C1–C15	88.01	76.37	C1–C22	74.02	64.92
C4–C22	86.70	74.03	C4–C20	74.65	61.97	C5–C22	74.02	64.92
C6–C15	84.54	73.38	C5–C17	87.87	73.60	C6–C15	84.17	71.78
C1–N2	70.79	63.14	C15–C20	73.37	63.83	C1–N2	70.29	62.29
C1–N16	96.68	85.28	C1–N3	89.81	77.68	C1–N16	96.80	85.39
C1–N21	63.55	56.93	C1–N6	91.52	77.52	C3–N2	77.40	68.53
C3–N2	82.80	71.52	C4–N3	90.63	77.96	C3–N21	77.00	68.08
C4–N7	82.80	71.52	C4–N14	63.45	55.96	C4–N7	77.40	68.53
C5–N7	70.79	63.14	C5–N16	87.24	74.00	C4–N21	77.00	68.08
C5–N21	63.55	56.93	C7–N6	98.32	84.27	C5–N7	70.29	62.29
C6–N2	67.42	61.14	C7–N14	66.83	58.30	C5–N17	112.30	96.55
C6–N7	67.42	61.14	C15–N16	74.36	65.67	C6–N2	69.05	63.64
C15–N16	67.15	79.26	C17–N14	72.57	65.99	C6–N7	69.05	63.64
C15–N17	67.15	79.26	C17–N21	95.46	84.35	C15–N16	91.13	80.10
						C15–N17	91.13	80.10

### Thermodynamic stability

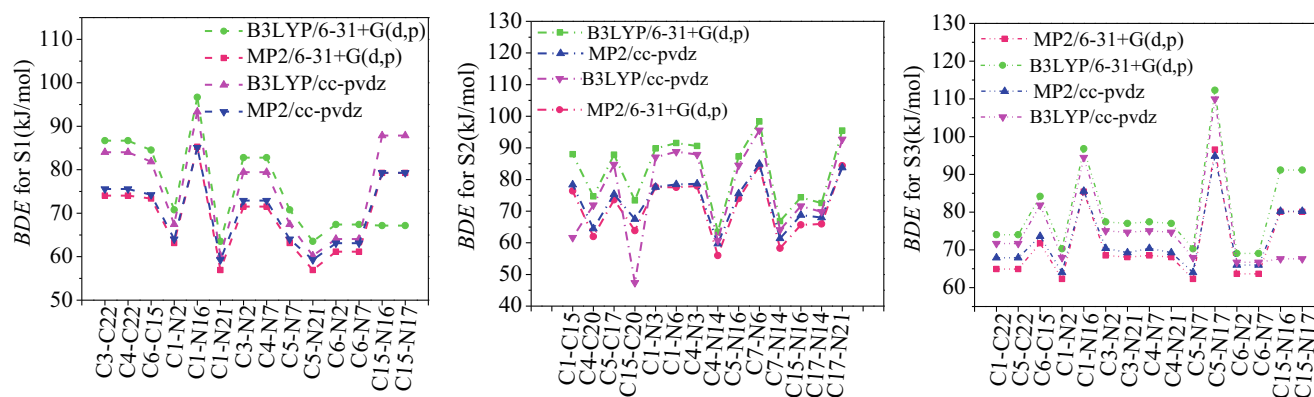
Table 5 lists the energies of the three isomers optimized at the B3LYP/6-31G (d) level.

Obviously, isomer 2 is the most thermodynamically stable of the isomers. The primary reason for this may be the relative bond strengths of the C–C and C–N bonds; the bond energies [50] for these two bonds are 83.2 and 72.9 kcal mol<sup>-1</sup>, respectively. Thus, generally, for any internal rearrangement of the atoms in a molecule, replacing a C–C with a C–N bond should be energetically disadvantageous by 10.3 kcal mol<sup>-1</sup> [50]. This means that isomer 2 should benefit from its energetically advantageous arrangement of atoms compared to isomers 1 and 3, and should be more stable than them by about 10.3 kcal mol<sup>-1</sup>.

If two isomers are compared that have the same numbers of each type of bond (e.g., isomer 1 and isomer 3), the molecule with fewer carbon atoms in the axial hexagons is found to be more stable. Of course, it should be pointed out that this stability is only based on a comparison of the relative energies. Actually, a C–C bond is not always stronger than a C–N bond in cage molecules—sometimes the dissociation energy of a C–N bond is even larger than that of a C–C bond; however, both of them are stronger than an N–N bond [50].

### Kinetic stability (bond-breaking energy)

Tables 6 and 7 show the bond-breaking energies for the three C<sub>7</sub>N<sub>5</sub>H<sub>11</sub> cages. All the bonds that could be broken are considered in the tables.



**Fig. 3a–c** Plots of bond versus the corresponding bond-breaking energy for isomers S1 (a), S2 (b), and S3 (c)



To highlight the relationship between the molecular structure and the bond-breaking energies, we plotted the data from Tables 6 and 7 in Fig. 3. It is evident that all of the bond energies calculated at the B3LYP/6-31+G(d,p) level of theory for the three isomers are the largest among the four different methods employed in this work, and the maximum difference in bond-breaking energy between the three  $C_7N_5H_{11}$  isomers obtained using the different methods is about  $10 \text{ kcal mol}^{-1}$ .

Apparently, at all levels of theory applied, most of the C–C bonds in isomer 1 have larger bond-breaking energies than the C–N bonds do in this isomer, except for the bonds C1–N16 and C5–N16. The weakest bond is the C–N bond. It is likely that the mechanism of pyrolysis for isomer 1 begins with the breaking of a C–N bond. All of the methods employed in the present work indicate that the dissociation energy of a C–C bond is not always larger than that of a C–N bond; for example, the bond dissociation energy of C1–N16 for isomer 1 is  $93.34 \text{ kcal mol}^{-1}$ , which is larger than that of C3–C22 ( $84.02 \text{ kcal mol}^{-1}$ ).

As indicated in Tables 6 and 7, some bond dissociation energies in isomer 1 and isomer 3 are the same because of the symmetry of their molecular structures. The strongest bond and weakest bond of isomer 1 are always the same, C1–N16 and C1–N21 (C5–N21), respectively. There is a special situation for isomers 2 and 3. The weakest bond in isomer 2 is C15–C20 according to B3LYP/cc-pvdz, and its dissociation energy is  $47.39 \text{ kcal mol}^{-1}$  which was verified repeatedly. The reason for this is not yet clear and warrants further investigation. Meanwhile, the weakest bond was C4–N14 when calculations were performed at the other three levels of theory.

Now let us turn to isomer 3. The strongest bond is the same at all four levels of theory, C5–N17, while the weakest is C6–N2 when calculated at the B3LYP/cc-pvdz or B3LYP/6-31+G(d,p) level and C5–N7 when calculated at the MP2/cc-pvdz or MP2/6-31+G(d,p) level. One of the reasons for these different results for the weakest bond may be that both of these bonds are easy to break so their dissociation energies are rather similar. Another reason may be the characteristics of the two methods. Interestingly, for the three molecules studied in the present work, the difference between the B3LYP dissociation energies calculated with different basis sets is about  $2\text{--}3 \text{ kcal mol}^{-1}$ , while it is  $1\text{--}2 \text{ kcal mol}^{-1}$  for the MP2 results, and the B3LYP dissociation energies are consistently higher than those of MP2 (presumably the most accurate values obtained in the study). It should be noted that the highest dissociation energy given at all levels of theory is that of the weakest C–N bond in isomer 3, which indicates that this isomer is the most stable with respect to dissociation.

## Conclusions

Three  $C_7N_5H_{11}$  cages have been investigated using quantum-chemical calculations. Comparison of the HOFs of the

different isomers revealed that they were all positive, indicating that a huge of energy will be released when each compound decomposes. Studies show that isomer 2, which contains the most C–C bonds, is usually more thermodynamically stable than the isomers with more C–N bonds, while isomer 3 is most stable with respect to bond dissociation energy. All of the results imply that these three  $C_7N_5H_{11}$  cage isomers are good candidates for potential HEDMs. The results of the present systemic comparative investigation should prove useful for the molecular structural design and synthesis of cage compounds in the future.

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