

## Stability of Carbon–Nitrogen Cages in 3-Fold Symmetry

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**Abstract:** Molecules consisting entirely of nitrogen have been studied extensively for their potential as high energy density materials (HEDM). One class of potential high-energy nitrogen molecules is the cage of three-coordinate nitrogen. Previous theoretical studies of cages  $N_x$  have shown that the most stable isomers are cylindrical molecules with 3-fold symmetry and triangular endcaps, but such molecules are not stable with respect to dissociation. In the current study, nitrogen cages are modified to include carbon atom substituents. Carbon atoms are studied for their potential to stabilize the nitrogen structures while maintaining significant levels of energy release from the molecules. Theoretical calculations are carried out on a sequence of high-energy cages with carbon and nitrogen. Density functional theory (B3LYP), perturbation theory (MP2 and MP4), and coupled-cluster theory (CCSD(T)) are used in conjunction with the correlation-consistent basis sets of Dunning. Stability trends as a function of molecule size are calculated and discussed.

### Introduction

Nitrogen molecules have been the subject of many recent studies because of their potential as high energy density materials (HEDM). An all-nitrogen molecule  $N_x$  can undergo the reaction  $N_x \rightarrow (x/2)N_2$ , a reaction that can be exothermic by 50 kcal/mol or more per nitrogen atom.<sup>1,2</sup> To be a practical energy source, however, a molecule  $N_x$  would have to resist dissociation well enough to be a stable fuel. Theoretical studies<sup>3–7</sup> have shown that numerous  $N_x$  molecules are not sufficiently stable to be practical HEDM, including cyclic and acyclic isomers with eight to twelve atoms. Cage isomers of  $N_8$  and  $N_{12}$  have also been shown<sup>7–10</sup> by theoretical calculations to be unstable. Experimental progress in the synthesis of nitrogen molecules has been very encouraging, with the  $N_5^+$  and  $N_5^-$  ions having been recently produced<sup>11,12</sup> in the laboratory. More recently, a network polymer of nitrogen has been produced<sup>13</sup> under very high-pressure conditions. Experimental successes have sparked theoretical studies<sup>1,14,15</sup> on other potential all-nitrogen molecules. More recent developments include the experimental synthesis of

high energy molecules consisting predominantly of nitrogen, including azides<sup>16,17</sup> of various heteroatoms and polyazido isomers<sup>18</sup> of compounds such as 1,3,5-triazine. Future developments in experiment and theory will further broaden the horizons of high energy nitrogen research.

The stability properties of  $N_x$  molecules have also been extensively studied in a computational survey<sup>19</sup> of various structural forms with up to 20 atoms. Cyclic, acyclic, and cage isomers have been examined to determine the bonding properties and energetics over a wide range of molecules. A more recent computational study<sup>20</sup> of cage isomers of  $N_{12}$  examined the specific structural features that lead to the most stable molecules among the three-coordinate nitrogen cages. Those results showed that molecules with the most pentagons in the nitrogen network tend to be the most stable, with a secondary stabilizing effect due to triangles in the cage structure. A recent study<sup>21</sup> of larger nitrogen molecules  $N_{24}$ ,  $N_{30}$ , and  $N_{36}$  showed significant deviations from the pentagon-favoring trend. Each of these molecule sizes has fullerene-like cages consisting solely of pentagons and hexagons, but a large stability advantage was found for molecules with fewer pentagons, more triangles, and an overall structure more cylindrical than spheroidal. Studies<sup>22,23</sup> of intermediate-sized molecules  $N_{14}$ ,  $N_{16}$ , and  $N_{18}$  also showed that the cage

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isomer with the most pentagons was not the most stable cage, even when compared to isomer(s) containing triangles (which have  $60^\circ$  angles that should have significant angle strain). For each of these molecule sizes, spheroidally shaped molecules proved to be less stable than elongated, cylindrical ones.

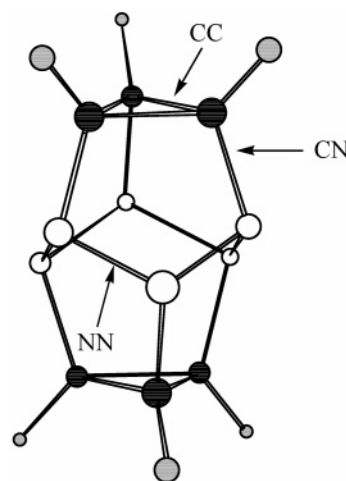
However, while it is possible to identify in relative terms which nitrogen cages are the most stable, it has been shown<sup>7</sup> in the case of  $N_{12}$  that even the most stable  $N_{12}$  cage is unstable with respect to dissociation. The number of studies demonstrating the instability of various all-nitrogen molecules has resulted in considerable attention toward compounds that are predominantly nitrogen but contain heteroatoms that stabilize the structure. In addition to the experimental studies<sup>16–18</sup> cited above, theoretical studies have been carried out that show, for example, that nitrogen cages can be stabilized by oxygen insertion<sup>24,25</sup> or phosphorus substitution.<sup>26</sup> The phosphorus study predicted the stability of a molecule of  $N_6P_6$ , but phosphorus is a high-mass atom that does not contribute appreciably to energy release. These atoms dilute the energy-per-unit-mass properties of the molecule. Therefore, in designing a viable HEDM, it is not only necessary to have a stable molecule but also desirable to minimize the number and mass of heteroatoms and thereby maximize energy production from the HEDM. In the current study, several molecules are studied whose structures are based on the most stable  $N_{12}$  and  $N_{18}$  but with carbon atoms (much lighter than phosphorus) substituted into the cage network. The stability of carbon–nitrogen cages is determined by theoretical calculations of the energies of various dissociation pathways of each molecule.

## Computational Details

Geometries are optimized with density functional theory<sup>27,28</sup> (B3LYP) and second-order perturbation theory<sup>29</sup> (MP2). Single energy points are calculated with fourth-order perturbation theory<sup>29</sup> (MP4(SDQ)) and coupled-cluster theory<sup>30</sup> (CCSD(T)). Multireference effects are calculated by complete active space (CASSCF(4,4)) calculations with MP2 energies included. Molecules are optimized in the singlet state, and dissociation intermediates are optimized in the triplet state, which is the ground state for all dissociations in this study. The basis sets are the double- $\zeta$  (cc-pVDZ), augmented double- $\zeta$  (aug-cc-pVDZ), and triple- $\zeta$  (cc-pVTZ) sets of Dunning.<sup>31</sup> Vibrational frequencies have been calculated at the MP2/cc-pVDZ level of theory for  $N_6C_6H_6$  and for all its dissociation intermediates. For the larger intact molecules, B3LYP/cc-pVDZ frequencies have been calculated. The Gaussian03 computational chemistry software,<sup>32</sup> and its Windows-based counterpart Gaussian03W, have been used for all calculations in this study.

## Results and Discussion

The first molecule under consideration in this study is a variation on the most stable  $N_{12}$  cage. The molecule has two triangular endcaps that have been replaced by carbon atoms. Including the hydrogens that are added for the fourth bond of carbon, this molecule has the formula  $N_6C_6H_6$  and is shown in Figure 1. The molecule has  $D_{3d}$  point group



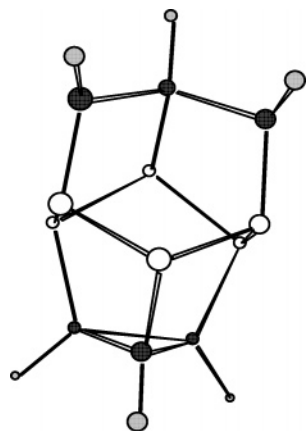
**Figure 1.**  $N_6C_6H_6$  molecule ( $D_{3d}$  point group symmetry). Symmetry-independent bonds are labeled. Nitrogen is shown in white, carbon in black, and hydrogen in gray.

**Table 1.** Bond-Breaking Energies for  $N_6C_6H_6$  Molecule<sup>a</sup>

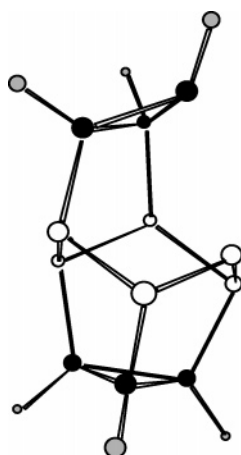
energy	geometry	bonds (see Figure 1)		
		CC	CN	NN
B3LYP/cc-pVDZ	B3LYP/cc-pVDZ	+68.4	+85.8	+21.3
MP2/cc-pVDZ	MP2/cc-pVDZ	+78.7	+105.5	+42.5
MP2(+ZPE)/cc-pVDZ	MP2/cc-pVDZ	+76.6	+102.5	+41.5
MP2(+free energy)/cc-pVDZ	MP2/cc-pVDZ	+74.6	+100.3	+39.7
CAS(4,4)/MP2/cc-pVDZ	MP2/cc-pVDZ	+83.3	+111.8	+49.9
MP2/aug-cc-pVDZ	MP2/aug-cc-pVDZ	+78.5	+106.5	+44.9
MP2/cc-pVTZ	MP2/cc-pVTZ	+81.7	+109.2	+45.2
MP4/cc-pVDZ	MP2/cc-pVDZ	+71.3	+96.1	+31.8
MP4/aug-cc-pVDZ	MP2/aug-cc-pVDZ	+70.6	+96.3	+33.3
CCSD(T)/cc-pVDZ	MP2/cc-pVDZ	+71.4	+93.0	+31.4

<sup>a</sup> Energies in kcal/mol.

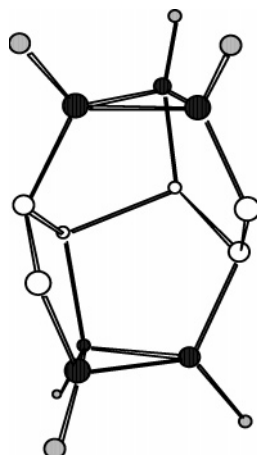
symmetry and three symmetry-independent bonds, and the intermediates for breaking each bond are shown in Figures 2–4. The dissociation energies for bond-breaking processes of  $N_6C_6H_6$  are shown in Table 1. (The molecule and all of its one-bond-breaking intermediates are been verified as local minima, and the effects of zero-point energy and free energy are shown in Table 1.) MP2 and B3LYP energies do not agree, with B3LYP giving lower bond dissociation energies. The most easily broken bond is the nitrogen–nitrogen (NN) bond, but even this bond has a dissociation energy of more than 30 kcal/mol at the CCSD(T)/cc-pVDZ level of theory, which is the most reliable method in this study. The MP4/cc-pVDZ results agree closely with CCSD(T). Basis set effects from diffuse functions (aug-cc-pVDZ) or higher angular momentum functions (cc-pVTZ) tend to increase the bond dissociation energies. Multireference effects on the dissociation energies have been calculated by CASSCF(4,4) calculations with MP2 corrections, resulting in increases in the dissociation energies by 5–8 kcal/mol. Since all of the bonds in the  $N_6C_6H_6$  have high dissociation energies, this molecule is probably a good candidate for a practical HEDM. However, this molecule is only 52% nitrogen by mass, and since nitrogen is the source of the energy release, it would be desirable to increase the percentage of nitrogen in the molecule if possible while maintaining stability.



**Figure 2.**  $N_6C_6H_6$  molecule, with a C–C bond broken. Nitrogen is shown in white, carbon in black, and hydrogen in gray.

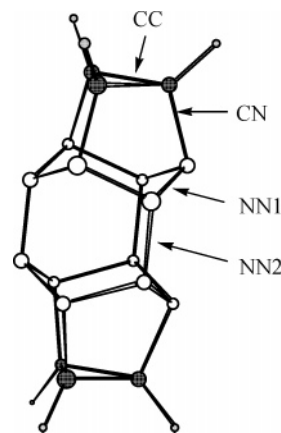


**Figure 3.**  $N_6C_6H_6$  molecule, with a C–N bond broken. Nitrogen is shown in white, carbon in black, and hydrogen in gray.



**Figure 4.**  $N_6C_6H_6$  molecule, with a N–N bond broken. Nitrogen is shown in white, carbon in black, and hydrogen in gray.

It is possible to design a molecule with the same carbon end-caps with two six-membered rings of nitrogen instead of only one. This molecule has a formula  $N_{12}C_6H_6$  and is shown in Figure 5. This molecule is 68% nitrogen by mass and more energetic than  $N_6C_6H_6$  as shown in Table 2, but is



**Figure 5.**  $N_{12}C_6H_6$  molecule ( $D_{3h}$  point group symmetry). Symmetry-independent bonds are labeled. Nitrogen is shown in white, carbon in black, and hydrogen in gray.

**Table 2.** Free Energies of Reaction for Molecules in This Study, Calculated by the B3LYP/cc-pVDZ Method

molecule	reaction	kcal/mol	kcal/g
$N_6C_6H_6$	$N_6C_6H_6 \rightarrow 3N_2 + C_6H_6$	−271.0	−1.7
$N_{12}C_6H_6$	$N_{12}C_6H_6 \rightarrow 6N_2 + C_6H_6$	−561.8	−2.3
$N_{12}C_9H_6$	$N_{12}C_9H_6 \rightarrow 6N_2 + (1/2)C_6H_6 + (1/4)C_{24}H_{12}$	−555.1	−2.0
$N_{18}C_{12}H_6$	$N_{18}C_{12}H_6 \rightarrow 9N_2 + (1/2)C_{24}H_{12}$	−840.8	−2.1
$N_6P_6$	$N_6P_6 \rightarrow 3N_2 + (3/2)P_4$ (ref 26)	−230.8	−0.9

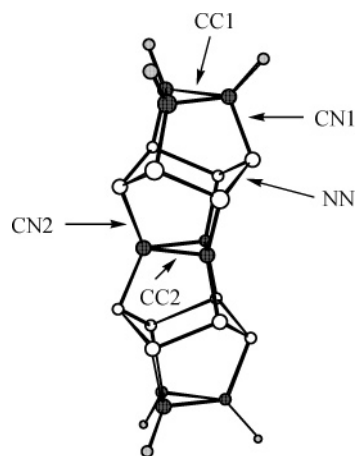
**Table 3.** Bond-Breaking Energies for  $N_{12}C_6H_6$  Molecule<sup>b</sup>

energy	geometry	bonds (see Figure 5)			
		CC	CN	NN1	NN2
B3LYP/cc-pVDZ	B3LYP/cc-pVDZ	+70.6	+76.8	<sup>a</sup>	<sup>a</sup>
MP2/cc-pVDZ	MP2/cc-pVDZ	+80.8	+104.0	+30.5	+86.2
MP4/cc-pVDZ	MP2/cc-pVDZ	+73.4	+95.6	+23.1	+75.3
MP2/aug-cc-pVDZ	MP2/aug-cc-pVDZ	+80.6	+105.1	+33.7	+88.9

<sup>a</sup> Geometry optimization was unsuccessful. <sup>b</sup> Energies in kcal/mol.

it stable with respect to dissociation? Bond-breaking energies are shown in Table 3 for the four symmetry-independent bonds (in  $D_{3h}$  symmetry). As with  $N_6C_6H_6$ , the weakest bond is the nitrogen–nitrogen bond (NN1) within a ring of nitrogen (as opposed to NN2, which connects the two rings of nitrogen). The bond-breaking energy is much lower than in the smaller molecule, 12 kcal/mol lower at the MP2/cc-pVDZ level of theory, and 9 kcal/mol at the MP4/cc-pVDZ level of theory. At the highest level of theory in this study, the molecule has less than 30 kcal/mol resistance to dissociation and is likely only a marginal candidate for HEDM. This is an effect similar to what was shown<sup>25</sup> for a series of carbon–oxygen-capped molecules with stacked six-membered rings of nitrogen. It seems that ring-stacking nitrogen upon nitrogen leads to weakening of N–N single bonds for large nitrogen cage structures.

Would separating the two nitrogen rings result in a stability enhancement for the molecule? Figure 6 shows a molecule with another triangle of carbon between the two rings of nitrogen. This molecule has the formula  $N_{12}C_9H_6$ , which is 60% nitrogen by mass. The molecule has  $D_{3h}$  point group symmetry and five symmetry-independent bonds. The dis-

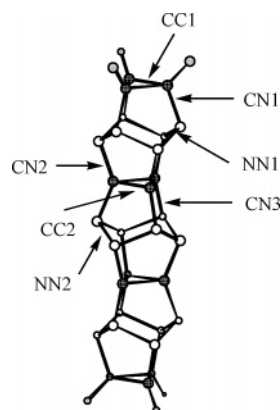


**Figure 6.**  $N_{12}C_9H_6$  molecule ( $D_{3h}$  point group symmetry). Symmetry-independent bonds are labeled. Nitrogen is shown in white, carbon in black, and hydrogen in gray.

**Table 4.** Bond-Breaking Energies for  $N_{12}C_9H_6$  Molecule<sup>b</sup>

energy	geometry	bonds (see Figure 6)				
		CC1	CN1	NN	CN2	CC2
B3LYP/cc-pVDZ	B3LYP/cc-pVDZ	<i>a</i>	+89.4	+15.0	+71.1	+70.1
MP2/cc-pVDZ	MP2/cc-pVDZ	+78.8	+108.8	+36.7	+89.1	+86.0
MP4/cc-pVDZ	MP2/cc-pVDZ	+71.1	+98.5	+25.3	+79.6	+76.2

<sup>a</sup> Geometry optimization was unsuccessful. <sup>b</sup> Energies in kcal/mol.



**Figure 7.**  $N_{18}C_{12}H_6$  molecule ( $D_{3d}$  point group symmetry). Symmetry-independent bonds are labeled. Nitrogen is shown in white, carbon in black, and hydrogen in gray.

sociation energies for each bond are shown in Table 4. For the weakest bond in both molecules ( $N_{12}C_9H_6$  and  $N_{12}C_9H_6$ ), which is a nitrogen–nitrogen bond, the additional ring of carbon results in 6 kcal/mol of additional stability at the MP2/cc-pVDZ level of theory (+36.7 versus +30.5 kcal/mol dissociation energy). At the MP4/cc-pVDZ level of theory, the stability advantage of the additional ring of carbon diminishes to about 2 kcal/mol (+25.3 versus +23.1 kcal/mol).

The structure of  $N_{12}C_9H_6$  can be extended with another ring of six nitrogens and a ring of three carbons to form a larger molecule with formula  $N_{18}C_{12}H_6$ . This molecule is shown in Figure 7 and consists of 63% nitrogen by mass. The molecule has seven symmetry-independent bonds between heavy atoms, and the dissociation energies for the

**Table 5.** Bond-Breaking Energies for  $N_{18}C_{12}H_6$  Molecules<sup>b</sup>

bonds (see Figure 7)	B3LYP/cc-pVDZ	MP2/cc-pVDZ
CC1	<i>a</i>	+78.8
CN1	+89.6	+109.0
NN1	+15.1	+36.7
CN2	+70.7	+88.9
CC2	+68.9	+85.6
CN3	+74.5	+92.2
NN2	+8.0	+30.1

<sup>a</sup> Geometry optimization was unsuccessful. <sup>b</sup> Energies in kcal/mol.

bonds are shown in Table 5. The results indicate that the weakest bond in the molecule is a nitrogen–nitrogen bond in the central ring of nitrogen atoms. Comparing MP2/cc-pVDZ results with the smaller  $N_{12}C_9H_6$  reveals that the molecule with three rings of nitrogen is less stable than the molecule with two.  $N_{18}C_{12}H_6$  can break an N–N bond more easily (by about 6 kcal/mol) than  $N_{12}C_9H_6$ . The  $N_{18}C_{12}H_6$  molecule is therefore unlikely to be a stable HEDM.

## Conclusion

Carbon is a viable heteroatom substituent in stabilizing  $N_{12}$  to form the stable  $N_6C_6H_6$ . However, lengthening schemes designed to extend the stabilizing features of  $N_6C_6H_6$  to larger, nitrogen-rich molecules result in molecules that are less stable than  $N_6C_6H_6$ . These larger molecules are therefore less likely to serve as a practical high energy density material (HEDM). As a substitute for nitrogen, the lighter carbon atoms have a less drastic effect on energy output than the heavier, previously studied phosphorus atom substituents. The  $N_6C_6H_6$  molecule is stable enough to serve as an HEDM, and it should have energy release properties much more favorable than  $N_6P_6$ .

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**Supporting Information Available:** MP2/cc-pVDZ optimized geometries for molecules and intermediates (coordinates in Å). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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