

Stability of N₁₈C₆H₆: Triangular versus Hexagonal Structure

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Large nitrogen cage molecules N_x have been previously shown to prefer elongated, cylindrical structures with triangular caps versus more spherical structures composed entirely of pentagons and hexagons. It was argued that this preference derived from the electronic properties of the nitrogen atoms, including the lone pairs. In the current study, the same structural comparison is carried out, with the substitution of C–H-bonding groups for six of the nitrogens. Various substitution patterns on the cylindrical (triangular) and spherical (hexagonal) frameworks are examined. Isomers of N₁₈C₆H₆ are studied by theoretical calculations to determine the relative stability of triangular versus hexagonal structures, as well as the stability effects of the substitution patterns on each framework. Hartree–Fock theory, density functional theory (PBE1PBE), and perturbation theory (MP2) are employed, in conjunction with the correlation-consistent basis sets of Dunning. Stability trends within each class of molecules and between the two classes of molecules are calculated and discussed.

Introduction

Nitrogen molecules have been the subjects 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 → (x/2)N₂, a reaction that can be exothermic by 50 kcal/mol or more per nitrogen atom.^{1,2} 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^{3–7} 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 N₈ and N₁₂ have also been shown^{7–10} by theoretical calculations to be unstable. Experimental progress in the synthesis of nitrogen molecules has been very encouraging, with the N₅⁺ and N₅[−] ions having been recently produced^{11,12} in the laboratory. More recently, a network polymer of nitrogen has been produced¹³ under very high-pressure conditions. Experimental successes have sparked theoretical studies^{1,14,15} on other potential all-nitrogen molecules. More recent developments include the experimental synthesis of high-energy molecules consisting predominantly of nitrogen, including azides^{16,17} of various molecules and polyazides^{18,19} of atoms and molecules, 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 survey²⁰ 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 study²¹ of cage isomers of N₁₂ 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 study²² of larger nitrogen molecules N₂₄, N₃₀, and N₃₆ 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^{23,24} of intermediate-sized molecules N₁₄, N₁₆, and N₁₈ also showed that the cage isomer with the most pentagons was not the most stable cage, even when compared to isomer(s) containing triangles (which have 60° 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, although it is possible to identify in relative terms which nitrogen cages are the most stable, it has been shown⁷ in the case of N₁₂ that even the most stable N₁₂ 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^{16–18} cited above, theoretical studies have been carried out that show, for example, that nitrogen cages can be stabilized by oxygen insertion^{25,26} or phosphorus substitution.²⁷

A study²⁸ of carbon–nitrogen cages showed that carbon substitution into an N₁₂ cage results in a stable N₆C₆H₆, but the only isomer considered was one in which the six carbon atoms replaced the nitrogen atoms in the two axial triangles of the original N₁₂. A further study²⁹ of several isomers of N₆C₆H₆ showed that, for substitutions of C–H-bonding groups into an N₁₂ cage, the most stable isomers were the ones with the largest number of C–N bonds. Also, the isomers with the highest number of C–N bonds also had the highest dissociation energies in the N–N bonds, which is significant because the N–N were weaker than other bonds in the cage. The strength of the N–N

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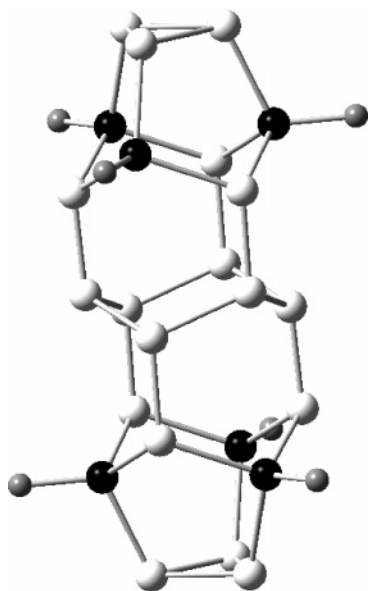


Figure 1. $N_{18}C_6H_6$ cage isomer T1 (D_{3d} point group symmetry). Nitrogen atoms are shown in white, carbon atoms in black, and hydrogen atoms in gray.

bonds, therefore, plays a key role in the overall stability of the molecules with respect to dissociation. Similar studies³⁰ have been carried out for cage isomers of $N_8C_8H_8$.

Isomers of the previously studied cages may be stable enough to be viable high-energy materials, but $N_6C_6H_6$ and $N_8C_8H_8$ only have 52% nitrogen content by mass. Because the decomposition of the nitrogen provides the energy release, it is preferable to have nitrogen structures that are richer in nitrogen. To that end, the current study involves a theoretical characterization of cage isomers of $N_{18}C_6H_6$, which are carbon-substituted versions of the previously studied N_{24} cages. The objective of the study is to determine the impact of various carbon substitution patterns on the stability of the molecule. The N_{24} cages chosen for study are the 2066P and 00(12)2 isomers from the previous N_{24} study. The 2066P isomer is a cylindrical cage with triangular end-caps, and the 00(12)2 isomer has hexagonal symmetry and is structurally analogous to the N_{24} fullerene. A total of seven isomers of $N_{18}C_6H_6$ are examined in this study.

Computational Methods

Geometries of the seven $N_{18}C_6H_6$ cages are optimized using Hartree–Fock theory, the PBE1PBE density functional method,³¹ and second-order Moller–Plesset theory³² (MP2). The correlation-consistent basis sets (cc-pVDZ and aug-cc-pVDZ) of Dunning³³ are used in this study. The Gaussian03 computational chemistry software package³⁴ (and its Windows counterpart Gaussian03W) are used for all calculations in this study.

Results and Discussion

Four isomers based on triangular structure are included in this study. They are designated T1, T2, T3, and T4 (collectively the “T-class” isomers), and they are shown in Figures 1–4. Three isomers based on hexagonal structure are included. They are designated H1, H2, and H3 (collectively the “H-class” isomers), and they are shown in Figures 5–7. All seven isomers are designed such that the structures have zero C–C bonds and, therefore, the maximum possible number of C–N bonds. Maximization of C–N bonds has been previously shown^{29,30} to be a stabilizing influence on carbon–nitrogen cages. Relative energies of the seven isomers have been calculated with the

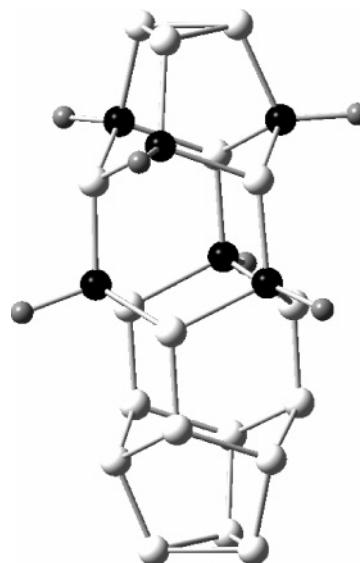


Figure 2. $N_{18}C_6H_6$ cage isomer T2 (C_{3v} point group symmetry). Nitrogen atoms are shown in white, carbon atoms in black, and hydrogen atoms in gray.

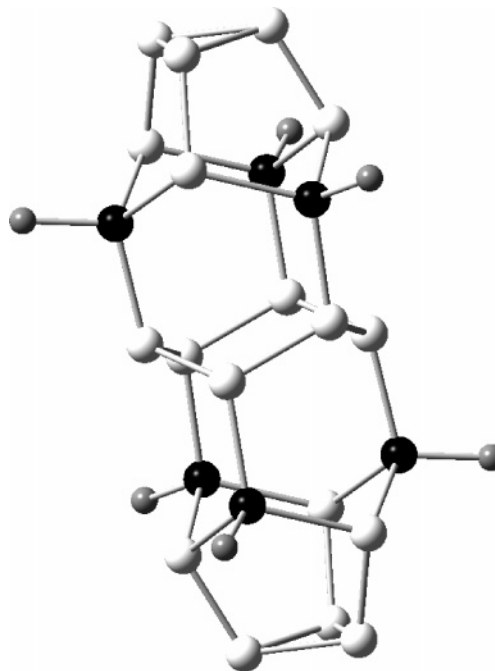


Figure 3. $N_{18}C_6H_6$ cage isomer T3 (D_{3d} point group symmetry). Nitrogen atoms are shown in white, carbon atoms in black, and hydrogen atoms in gray.

HF/cc-pVDZ, PBE1PBE/cc-pVDZ, MP2/cc-pVDZ, and PBE1PBE/aug-cc-pVDZ methods. Energies are shown in Table 1, and the four sets of calculations unanimously predict that isomer T4 is the most stable, followed by T3, T2, T1, H2, H3, and H1. The following stability trends are evident:

Stability within the T-Class of Isomers. The relative energies of the T-class isomers appear to be governed by two basic factors: (1) the presence or absence of fully alternated hexagons parallel to the long axis of the molecule, and (2) polarization of the triangular endcaps due to the proximity of neighboring carbon. Table 2 shows the Mulliken charges on the triangle nitrogen atoms in the T-class isomers. Each isomer has six triangle nitrogens, but due to 3-fold symmetry, the charges on all three nitrogens within a triangle are identical. Further, some of the T-class isomers are sufficiently symmetric

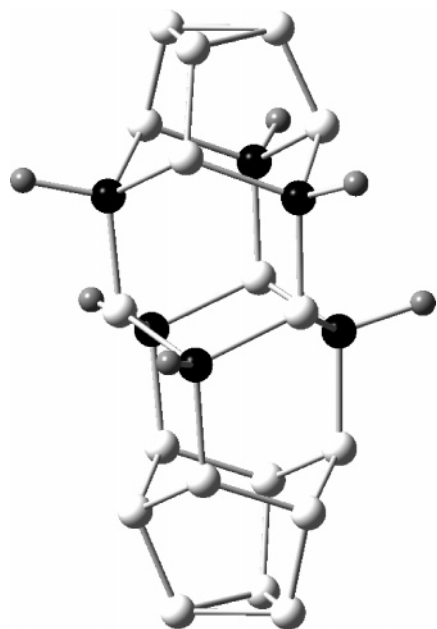


Figure 4. $N_{18}C_6H_6$ cage isomer T4 (C_{3v} point group symmetry). Nitrogen atoms are shown in white, carbon atoms in black, and hydrogen atoms in gray.

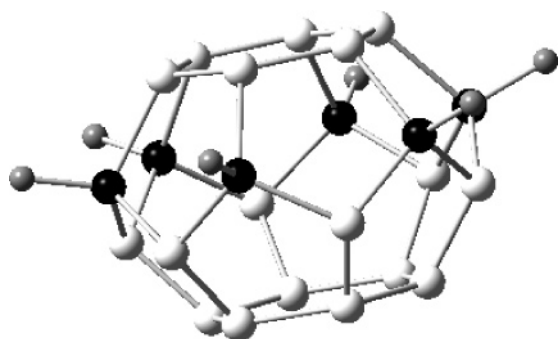


Figure 5. $N_{18}C_6H_6$ cage isomer H1 (C_{6v} point group symmetry). Nitrogen atoms are shown in white, carbon atoms in black, and hydrogen atoms in gray.

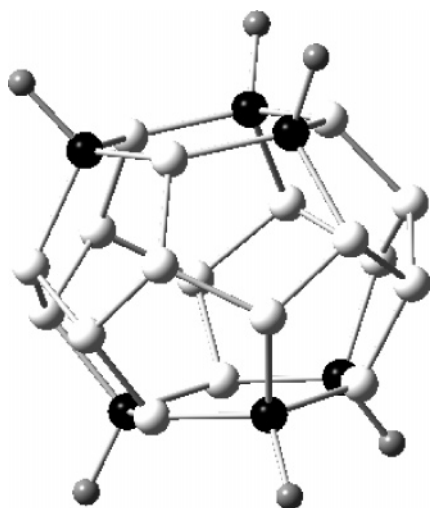


Figure 6. $N_{18}C_6H_6$ cage isomer H2 (D_{3d} point group symmetry). Nitrogen atoms are shown in white, carbon atoms in black, and hydrogen atoms in gray.

that the two triangles are also identical to each other. Note that T1 and T2 have higher negative charges than T3 and T4. This is because T1 and T2 have carbons that are directly bonded to the triangle nitrogens. The difference in electronegativity

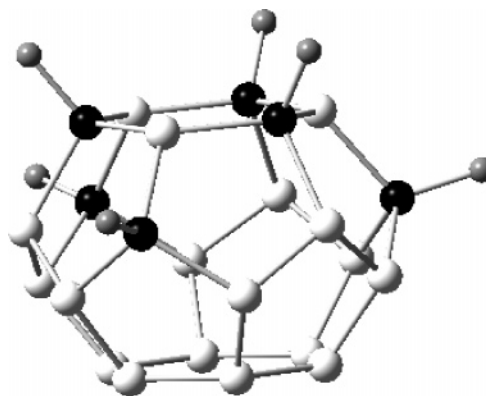


Figure 7. $N_{18}C_6H_6$ cage isomer H3 (C_{3v} point group symmetry). Nitrogen atoms are shown in white, carbon atoms in black, and hydrogen atoms in gray.

between carbon and nitrogen causes the negative charge on the nitrogen. Because the triangle nitrogens are also bonded directly to each other, the close proximity of negatively charged nitrogens causes a repulsive interaction that is destabilizing. This causes isomers T3 and T4, whose carbons are farther from the triangles, to be more stable than T1 and T2.

Influence of the Fully Alternated Hexagon. The presence of fully alternated hexagons also appears to be a stabilizing influence. A fully alternated hexagon is a ring of six atoms bonded in the sequence C–N–C–N–C–N. All four T-class isomers have these hexagons around the circumference of the cylinder, but only T2 and T4 have additional alternated hexagons parallel to the long axis of the molecule. C–N bonds are stronger than N–N bonds, and clustering large numbers of these bonds in close proximity has a stabilizing effect on the molecule as a whole. As a result, T2 is more stable than T1, and T4 is more stable than T3.

The effects of the CNCNCN hexagon can also be seen in the energies of the H-class isomers. The H-class frame only has two hexagons, and the three isomers in the study represent the three cases of zero, one, and two fully alternated hexagons. Isomer H1 has no C–N bonds in the hexagons and is the least stable of the H-class isomers. Isomer H2 is the exact opposite; all the carbons have been positioned in the hexagons for full alternation. Consequently, isomer H2 is much more stable than isomer H1. The effect is further illustrated by isomer H3, which is a sort of structural hybrid between H1 and H2. Isomer H3 has structural features of both H1 and H2, one alternated hexagon and a stability intermediate between H1 and H2.

T-Class Isomers versus H-Class Isomers. In the previous study²² on N_{24} cages, the T-class structure (designated 2066P) is more stable than the H-class structure (designated 00(12)2) by, for example, 112 kcal/mol at the MP2/cc-pVDZ level of theory. In that study, the cause of the energy difference was postulated to lie in the electronic structure of the nitrogen atom and the structure of nitrogen's preferred bonding environment. If that is so, then carbon substitution should narrow the energy gap between the two structures. If a comparison is made between the most stable T-class isomer of $N_{18}C_6H_6$, namely T4, and the most stable H-class isomer, namely H2, it is shown in Table 1 that the energy difference is 79 kcal/mol. This represents a roughly 30% reduction in relative energy between the two isomers. Carbon substitution does, in fact, narrow the gap between isomers, and further carbon substitution would likely narrow the gap further. However, because further carbon substitution would also dilute the nitrogen content and reduce the energy-producing capability of the molecules, it is likely

TABLE 1: Relative Energies of the N₁₈C₆H₆ Cages (Energies in kcal/mol)

	T1	T2	T3	T4	H1	H2	H3
HF/cc-pVDZ	+30.7	+18.8	+2.9	0.0	+91.6	+39.9	+62.2
PBE1PBE/cc-pVDZ	+37.2	+20.0	+5.2	0.0	+98.8	+53.4	+69.7
PBE1PBE/aug-cc-pVDZ	+37.8	+19.3	+6.6	0.0	+98.2	+52.1	+69.0
MP2/cc-pVDZ	+48.7	+23.6	+7.4	0.0	+125.7	+79.3	<i>a</i>

^a Geometry optimization is dissociative.

TABLE 2: Mulliken Charges on Nitrogen Atoms of the Triangles in T-Class Isomers of N₁₈C₆H₆ (Calculated with the MP2/cc-pVDZ Method)^a

isomer	charges
T1	-0.15
T2	-0.16, -0.10
T3	-0.05
T4	-0.04, +0.01

^a Where two values are specified, each value applies to one triangle only. Where only one value is specified, the two triangles are equivalent by symmetry.

TABLE 3: Energies of Detonation Reactions for N₂₄ and N₁₈C₆H₆ Isomers (Calculated with the PBE1PBE/cc-pVDZ Method)

molecule	reaction ^a	kcal/mol	kcal/g
T-class N ₂₄	N ₂₄ → 12 N ₂	889.6	2.65
T1	N ₁₈ -C ₆ H ₆ → 9N ₂ + C ₆ H ₆	515.6	1.56
T2	N ₁₈ -C ₆ H ₆ → 9N ₂ + C ₆ H ₆	498.5	1.51
T3	N ₁₈ -C ₆ H ₆ → 9N ₂ + C ₆ H ₆	483.6	1.47
T4	N ₁₈ -C ₆ H ₆ → 9N ₂ + C ₆ H ₆	478.4	1.45
H-class N ₂₄	N ₂₄ → 12N ₂	987.5	2.94
H1	N ₁₈ -C ₆ H ₆ → 9N ₂ + C ₆ H ₆	577.2	1.75
H2	N ₁₈ -C ₆ H ₆ → 9N ₂ + C ₆ H ₆	531.8	1.61
H3	N ₁₈ -C ₆ H ₆ → 9N ₂ + C ₆ H ₆	548.2	1.66

^a For detonation energies with H₂ and graphite instead of benzene, increase the above results by 49.0 kcal/mol, the heat of formation of benzene (ref 35).

that molecules with a T-class structure would be the most promising candidates for high-energy materials.

Impact of Carbon on Detonation Energies. Table 3 shows detonation energies for all seven N₁₈C₆H₆ cages, along with the T-class and H-class analogues of N₂₄. The reaction energies in Table 3 are calculated as the explicit energy differences between reactant and product molecules in the stated reactions at the PBE1PBE/cc-pVDZ level of theory. What is the impact of substituting one-fourth of the nitrogen atoms with carbon? The loss of 25% of the nitrogen causes energy release losses of approximately 40–45% for both T-class and H-class molecules. Because the energy release comes predominantly from the nitrogen, the loss of 25% of the nitrogen should account for a roughly 25% drop in detonation energy. The remaining energy loss comes from the stabilization of the reactant cage molecules resulting from the replacement of N–N bonds in the structure with the much stronger C–N bonds. Using standard bond enthalpies³⁵ of 39.0 kcal/mol for N–N and 72.9 for C–N, the N₂₄ cages have total binding energy of 1404 kcal/mol, whereas the cage network of N₁₈C₆H₆ has a total binding energy of 1709 kcal/mol. The N₂₄ is less tightly bound by roughly 18%, which accounts for the remaining drop in detonation energies for the more tightly bound N₁₈C₆H₆. Carbon substitution in the nitrogen network causes stabilization of the cage and destabilization of the detonation products, both of which contribute to the decrease in overall detonation energy.

Conclusion

Seven cage isomers of N₁₈C₆H₆ have been studied by theoretical calculations to determine the structural features that

lead to stable molecules. The following trends have been observed: (1) triangles consisting of polarized nitrogen atoms are destabilizing to T-class structures, (2) the alternated CNC–NCN hexagon is a stabilizing feature for both T-class and H-class structures, (3) carbon substitution reduces the relative energies between the two types of structural isomers, and (4) carbon substitution decreases detonation energy to a degree greater than the percentage of carbon substitution, because the C–N bonds stabilize the N₁₈C₆H₆ structure. The structural features determined in this study may lead to the design of even more stable high-energy materials in the future.

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Supporting Information Available: Geometries for all seven N₁₈C₆H₆ isomers are available as Supporting Information. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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