Trends in Stability for N$_{18}$ Cages

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Nitrogen molecules N$_x$ have been extensively studied for their potential as high energy density materials (HEDM). Cages of three-coordinate nitrogen have been studied to determine the structural features that result in the most stable isomers. N$_{12}$ cages, for example, have been shown to follow a general trend that molecules with more pentagons in the network are more stable than other molecules. Larger N$_x$ cages (24 or more atoms) do not follow this trend, favoring cylindrical structures over spherical ones with larger numbers of pentagons. To determine which trends intermediate-sized N$_x$ cages follow, a series of N$_{18}$ cages are studied by theoretical calculations of their stability. Geometries are optimized by using Hartree−Fock theory and perturbation theory (MP3), with single energies calculated with the fourth-order perturbation theory (MP4). The correlation-consistent CC-PVDZ basis of Dunning is employed. The major result is a loose trend favoring pentagons, with the most stable molecules being the ones with an optimal combination of pentagons and triangles.

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)N$_2$, 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 N$_8$ and N$_{12}$ 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 N$_5^+$ and N$_5^-$ ions having been recently produced[11,12] in the laboratory. Those experimental successes have sparked theoretical studies[13,14] on other potential all-nitrogen molecules, and future developments in experiment and theory will further broaden the horizons of all-nitrogen research.

The stability properties of N$_x$ molecules have also been extensively studied in a computational survey[15] 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[16] 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[17] 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.

The current study is an examination of stability trends at an intermediate size, namely N$_{18}$. Do the N$_{18}$ cages favor large numbers of pentagons (as with N$_{12}$) or do other isomers have the stability advantage (as with N$_{24}$ and larger molecules)? Theoretical calculations of a wide variety of N$_{18}$ molecules are conducted to address this question. Such cages have only N−N single bonds between three-coordinate nitrogen atoms, and the surface of each cage consists of a network of polygons. For the purpose of this study, the polygons shall be limited to triangles, squares, pentagons, and hexagons. For each molecule, n_3, n_4, n_5, and n_6 shall represent the number of three-, four-, five-, and six-sided polygons, respectively, in that molecule. Within that framework, the polygons in each N$_{18}$ molecule are subject to the following mathematical bounds:

$$3n_3 + 2n_4 + n_5 = 12 \qquad \text{(Euler's theorem)} \qquad (1)$$

$$n_3 + n_4 + n_5 + n_6 = 11$$
$$\text{(because each molecule has 18 atoms)} \quad (2)$$

The relationships between stability and the various types of polygons will indicate which structural features tend to stabilize an all-nitrogen cage.

Computational Details

Geometries are optimized by using Hartree−Fock (HF) theory and third-order Moller−Plesset perturbation theory[18] (MP3). (Several geometry optimizations failed for MP2, which has a bond-lengthening effect relative to HF theory, and this lengthening of bonds can lead to dissociative geometry optimizations.) A limited set of geometry optimizations has been carried out with the B3LYP density functional method,[19,20] limited because B3LYP suffers from optimization failures[16] due to bond lengthening just as MP2 does. Single-point energies are calculated with fourth-order Moller−Plesset perturbation theory[18]

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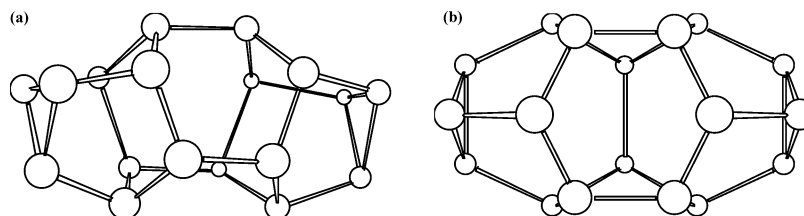[‡] Department of Physical Sciences.

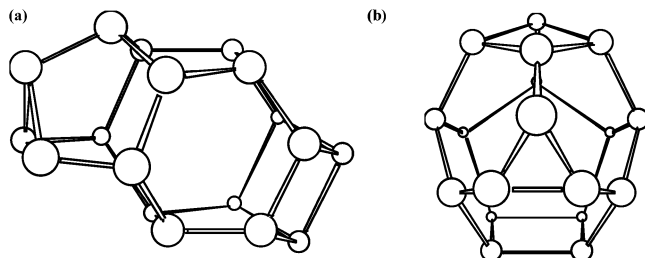**Figure 1.** (a) N_{18} isomer 2063A (D_{3h} symmetry point group) and (b) N_{18} isomer 2063B (C_{2v} symmetry point group).

Figure 2. (a) N_{18} isomer 1253A (C_s symmetry point group) and (b) N_{18} isomer 1253B (C_s symmetry point group).
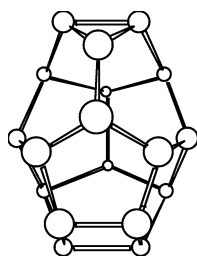

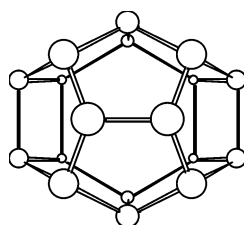**Figure 3.** N_{18} isomer 1172 (C_s symmetry point group).

Figure 4. N_{18} isomer 0281 (C_{2v} symmetry point group).

Figure 5. N_{18} isomer 3035 (C_s symmetry point group).

Figure 6. (a) N_{18} isomer 2144A (C_2 symmetry point group) and (b) N_{18} isomer 2144B (C_{2v} symmetry point group).

Figure 7. N_{18} isomer 0362 (C_{2v} symmetry point group).

Figure 8. (a) N_{18} isomer 1334A (C_s symmetry point group) and (b) N_{18} isomer 1334B (C_{3v} symmetry point group).

(MP4(SDQ)). The basis set[21] is the correlation-consistent double-ζ (cc-pVDZ) of Dunning. Previous studies of nitrogen cages have shown that basis set effects on isomer energies are not substantial. Calculations in this study are performed with the Gaussian 98 and Gaussian 03 quantum chemistry software packages.[22,23]

Results and Discussion

Eighteen molecules in all are covered by this study, with widely varying numbers of triangles, squares, pentagons, and hexagons. Each molecule shall be referred to by its $n_3n_4n_5n_6$ polygon counts. In addition to the variations in polygon counts, this study also includes five pairs of molecules with the same polygon counts but different structures. Calculations on these "fraternal twins" serve to show the importance of the arrangement of the polygons. Within each fraternal twin pair, the more stable of the two isomers is designated "A" and the other is designated "B". Structures of the 18 molecules are illustrated in Figures 1−13.

Relative energies of the 18 molecules are shown in Table 1. Results are shown from HF/cc-pVDZ and MP3/cc-pVDZ geometry optimizations, along with single-point energies with
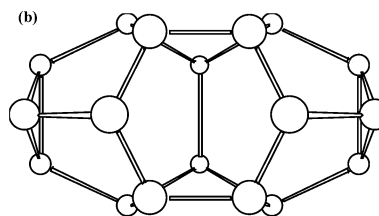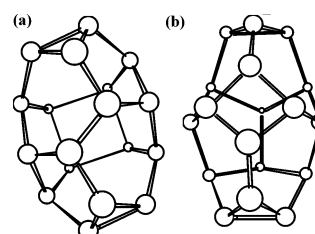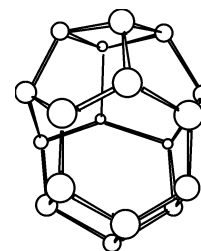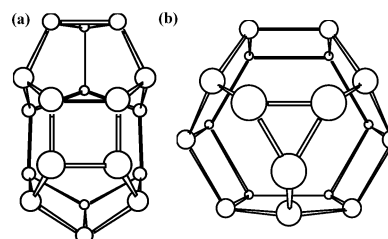
both geometries at the MP4/cc-pVDZ level of theory. It is interesting that HF and MP3 geometry optimizations give very similar relative energies between isomers. It should be noted that this is NOT because of any redundancy between HF and MP3 geometries. Table 2 shows a comparison between HF and MP3 bond lengths for the 2063A and 0605 isomers. MP3 bond lengths are consistently longer than HF bond lengths by 0.02− 0.06 Å. Imposing this bond lengthening effect on two N_{18} isomers apparently has very little effect on the energy difference between them. Whether HF, MP3, or MP4 energies are considered, several general trends are evident.

Pentagons: The most stable structures are 2063A and 2063B, even over 1172 and 0281, which have more pentagons. The
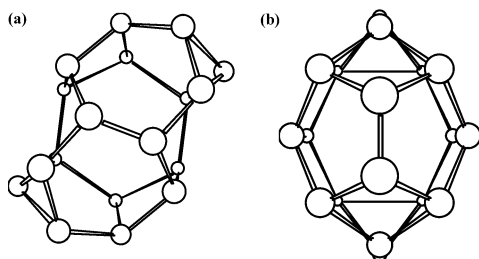
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Figure 9. (a) N$_{18}$ isomer 2225A (C_2 symmetry point group) and (b) N$_{18}$ isomer 2225B (C_{2v} symmetry point group).
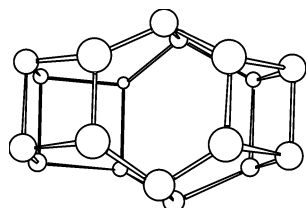
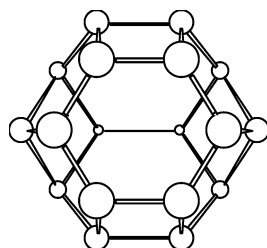**Figure 10.** N$_{18}$ isomer 0524 (C_{2v} symmetry point group).

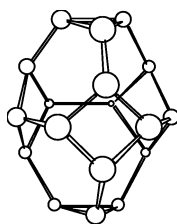**Figure 11.** N$_{18}$ isomer 0443 (C_{2v} symmetry point group).

Figure 12. N$_{18}$ isomer 2306 (D_{3h} symmetry point group).

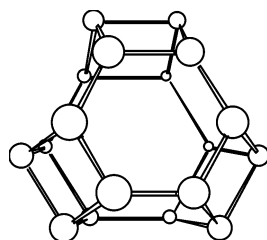**Figure 13.** N$_{18}$ isomer 0605 (D_{3h} symmetry point group).

pentagon stability trend seen for N$_{12}$ is not followed for N$_{18}$. With respect to the pentagons, there exists a "stability peak" at $n_5 = 6$ with stability diminishing above or below six pentagons. Molecules with five, seven, and eight pentagons follow 2063A and 2063B as next most stable. For $n_5 < 5$, the pentagon trend is followed, as shown by molecules with two to four pentagons being significantly more stable than molecules with none at all. A simple pentagon trend does not exist for N$_{18}$; the more complex behavior of the larger N$_x$ molecules is evidenced by N$_{18}$. N$_{18}$ is showing evidence of the effect of pyramidalization of the nitrogen, whereby an isomer with too many pentagons becomes too spheroidal. A cylindrical structure with fewer pentagons can provide a better environment for nitrogen to pyramidalize than a spheroidal structure with more pentagons.

TABLE 1: Relative Energies (kcal/mol) of N$_{18}$ Isomers^a

isomer	HF	MP3	MP4//HF	MP4//MP3
2063A	0.0	0.0	0.0	0.0
2063B	+20.6	+21.1	+19.6	+19.5
1253A	+34.9	+36.9	+36.9	+36.7
1172	+37.9	+40.1	+40.4	+39.8
0281	+50.1	+54.7	+55.5	+55.6
3035	+63.5	+60.6	+60.1	+58.3
2144A	+70.2	+69.7	+69.7	+68.0
0362	+74.8	+76.8	+77.3	+77.3
1334A	+80.1	+80.6	+80.7	+80.4
2144B	+85.1	+82.5	+82.4	+80.7
1253B	+85.9	+86.7	+86.8	+86.0
2225A	+95.6	+93.0	+93.2	+91.6
0524	+100.2	+101.0	+102.2	+101.9
0443	+121.0	+122.0	+122.0	+121.6
1334B	+126.4	+125.7	+126.0	+125.0
2225B	+131.4	+127.2	+127.1	+125.5
2306	+164.6	+161.3	+162.9	+160.1
0605	+185.4	+185.8	+189.1	+188.0

^{a} Isomers are indicated by their polygon counts $n_3n_4n_5n_6$, with "A" and "B" designations for pairs of molecules with identical polygon counts. All calculations used the cc-pVDZ basis set.

TABLE 2: Bond Lengths (Å) from HF/cc-pVDZ and MP3/cc-pVDZ Geometry Optimizations for the 2063A and 0605 Isomers of N$_{18}$

	HF	MP3
2063A symmetry-independent bonds:		
Triangle bond	1.442	1.506
Pentagon-pentagon edge	1.416	1.444
Pentagon-hexagon edge	1.426	1.466
Hexagon-hexagon edge	1.434	1.469
0605 symmetry-independent bonds:		
Square-hexagon (axial) edge	1.456	1.508
Square-hexagon (equatorial) edge	1.442	1.487
Hexagon-hexagon edge	1.426	1.460
Square-square edge	1.460	1.511

Triangles: As is the case with the N$_{12}$ molecules, there is a secondary stabilizing trend favoring triangles. For molecules with equal numbers of pentagons, the molecule with the most triangles is the most stable. All such comparisons within the molecule set in this study agree with the triangle-favoring trend, including the 2063A/2063B pair versus 0362, the 2144A/2144B pair versus 0443, 3035 versus both members of the 1334A/1334B pair, and 2306 versus 0605. In each case, the stability advantage belongs to the molecule(s) with the larger number of triangles. The reasons for this favoring have been discussed previously,[16] the central point being the exchange of two triangles and a hexagon for three squares, which is required if the number of pentagons is to remain equal between two isomers. Although the 60° angles of the triangles are individually more strained than the 90° angles of the squares, the exchange of polygons requires that the six strained angles of the two triangles be exchanged for the twelve strained angles of the three squares. This unfavorable exchange causes the isomer with the squares to be less stable.

"Fraternal Twins": Five pairs of fraternal twins have been examined in the study, pairs of molecules with identical $n_3n_4n_5n_6$ polygon counts but different arrangements of the polygons. Table 3 shows the stability data for each pair of fraternal twins in this study, with a comparison to structural features of the molecules. A trend emerges between the relative stability of molecules and the number of pentagons that are adjacent to each of the molecules' triangles. In every case in which the number of pentagons adjacent to triangles is different, the molecule with more pentagons around the triangles is more stable (isomer "A"). In fact, the effect is to some degree cumulative, that is, the

TABLE 3: Structural Comparisons between "Fraternal Twin" Isomers of N_{18}[a]

	stability advantage for "A"		pentagons around each triangle	
isomer pair	MP4//HF	MP4//MP3	isomer A	isomer B
2063A/2063B	19.6	19.5	3	2
1253A/1253B	49.9	49.3	2	0
2144A/2144B	12.7	12.7	1	1
1334A/1334B	45.3	44.6	2	0
2225A/2225B	33.9	33.9	1	0

[a] Within each pair, the most stable isomer is designated "A" and the other "B" (energies in kcal/mol)

TABLE 4: Comparison of B3LYP, HF, MP3, and MP4 Energies (kcal/mol) for Selected N_{18} Isomers[a]

	HF	MP3	B3LYP	MP4//HF	MP4//MP3	MP4//B3LYP
2063A	0.0	0.0	0.0	0.0	0.0	0.0
2063B	+20.6	+21.1	+13.2	+19.6	+19.5	+19.6
0281	+50.1	+54.7	+41.8	+55.5	+55.6	+55.6
0524	+100.2	+101.0	+86.7	+102.2	+101.9	+103.3

[a] All calculations used the cc-pVDZ basis set.

magnitude of the stability difference increases as the difference in the number of pentagons around the triangles increases. (One of the pairs of fraternal twins, 2144A/B, has the same number of pentagons around the triangles. This twin pair also has the smallest stability difference.) The pentagon−triangle substructure is a stabilizing feature of the N_{18} molecules, as it was shown to be between the 2066P and 2066H isomers in the previous study of N_{24} molecules.[17]

Although a full set of B3LYP optimized N_{18} geometries is unavailable due to bond lengthening in B3LYP, an effect that has been documented previously,[16] a limited set has been carried out, and the results are shown in Table 4. For these isomers, the B3LYP energies are somewhat closer together than for HF or MP3, but the magnitude of the energy differences is not large enough to affect the isomer trends discussed above. In any event, Table 4 also shows that when B3LYP optimized geometries are used for MP4 single-point energies, the results are essentially the same as for MP4 single-point energies with HF or MP3 geometries. Also, basis set effects are not anticipated to be significant, as shown previously for the larger N_{24} molecules.[17]

Conclusion

These N_{18} molecules show the complex stability behavior of their larger cousins, such as N_{24}. N_{18} has a pentagon stability trend, but it is more loosely obeyed than for N_{12}. At the N_{18} molecule size, the pyramidalization of the nitrogen plays a significant role in the stability ordering of the molecules. This pyramidalization effect causes cylindrical structures with fewer pentagons to be more stable than spheroidal structures that tend to have more planar rather than pyramidal environments for the nitrogen atoms. Triangles, despite having strained 60° angles, have a secondary stabilizing effect, a result seen for both N_{12} and N_{24}. Triangles and pentagons have also been shown to work together such that triangle−pentagon substructures lead to enhanced stability of the N_{18} molecules.

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