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Cage Isomers of N_{14} and N_{16}: Nitrogen Molecules That Are Not a Multiple of Six

Douglas L. Strout*

Department of Physical Sciences, Alabama State University, Montgomery, Alabama 36101

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Molecules consisting entirely or predominantly of nitrogen are the focus of much research for their potential as high energy density materials (HEDM). Recent theoretical predictions on cage stability for N_{12}, N_{18}, N_{24}, N_{30}, and N_{36} indicate that the most thermodynamically stable isomer has 3-fold symmetry (D_{3h} or D_{3d} symmetry point group). Such molecules have a triangle−pentagon bonding group on each end with a band of hexagons around the midsection. However, the existence of this symmetric isomer depends on the number of nitrogen atoms being a multiple of six. In the current study stability trends are addressed for two molecule sizes where this symmetric option does not exist, namely, N_{14} and N_{16}. Isomer energies for these molecules are calculated using Hartree−Fock theory, density functional theory (B3LYP), and perturbation theory (MP4) along with the correlation-consistent basis sets of Dunning. At each molecule size the most stable cage is identified, and the structural features leading to cage stability are 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 $N_x \rightarrow (x/2)\ N_2$, 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. A theoretical study[18] of cages of N_{18} also showed a preference for cylindrical molecules, and each of these studies (on N_{12}, N_{18}, N_{24}, N_{30}, and N_{36}) revealed that the most stable cage isomer at each molecule size is cylindrical with a 3-fold axis of symmetry (D_{3d} or D_{3h} point group).

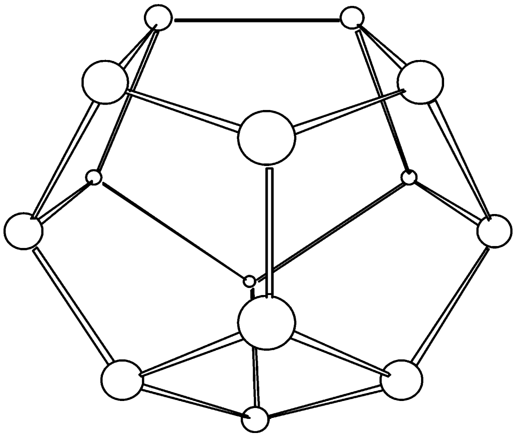

Figure 1. N_{14} isomer 0360 (D_{3h} point group symmetry).

However, the geometry of those cages depends on the number of nitrogen atoms being a multiple of six, since each cage has a triangle at each end with rings of six nitrogen atoms in between. Which nitrogen cage is most stable when the number of atoms is not a multiple of six? In the current study, cage isomers of N_{14} and N_{16} will be examined to determine which cage is the most stable and to determine the structural features that tend to stabilize cages at those sizes. The preferred arrangements of triangles, squares, pentagons, and hexagons for N_{14} and N_{16} are necessarily different from those studied previously. For each size a variety of cages will be studied that meet the following required mathematical boundaries (n_3, n_4, n_5, and n_6 refer to the number of three-, four-, five-, and six-membered polygons, respectively)

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

$$n_3 + n_4 + n_5 + n_6 = (x/2) + 2 \quad [x = \text{number of atoms composing the cage}] \quad (2)$$

The total number of polygons ($n_3 + n_4 + n_5 + n_6$) in each cage is 9 for N_{14} and 10 for N_{16}.

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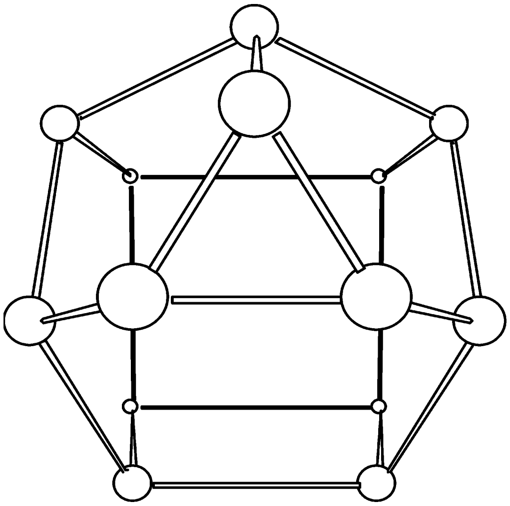

Figure 2. N_{14} isomer 1251 (C_s point group symmetry).

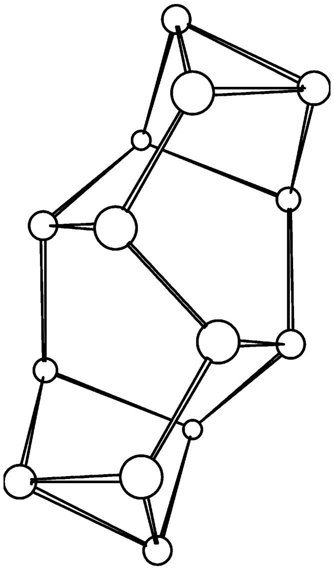

Figure 3. N_{14} isomer 2223 (C_2 point group symmetry).

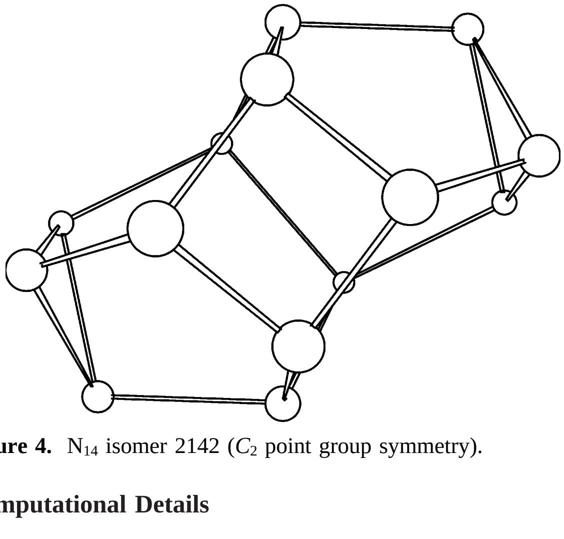

Figure 4. N_{14} isomer 2142 (C_2 point group symmetry).

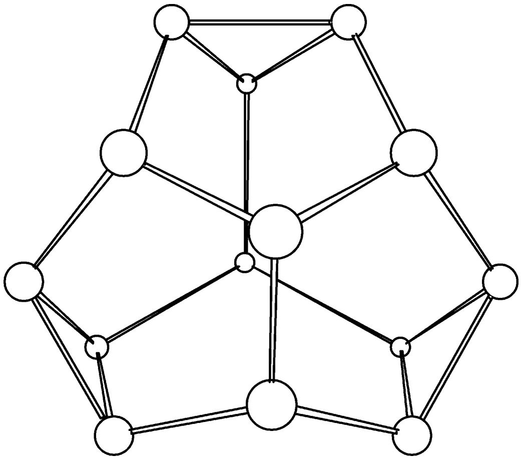

Figure 5. N_{14} isomer 3033 (C_{3v} point group symmetry).

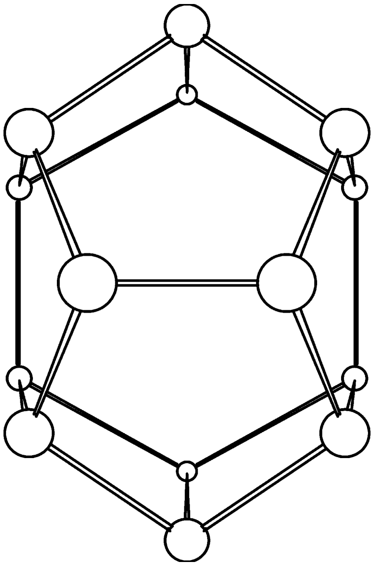

Figure 6. N_{14} isomer 0441 (C_{2v} point group symmetry).

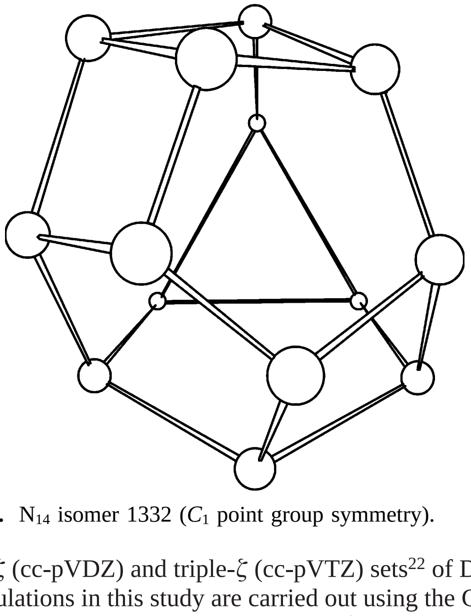

Figure 7. N_{14} isomer 1332 (C_1 point group symmetry).

Computational Details

Geometry optimizations were carried out using Hartree–Fock theory as well as the B3LYP density functional method.[19,20] (Some of the B3LYP optimizations are dissociative, a problem previously documented for other nitrogen cages.) Single energy points are carried out using fourth-order perturbation theory[21] (MP4(SDQ)). The basis sets are the correlation-consistent double-ζ (cc-pVDZ) and triple-ζ (cc-pVTZ) sets[22] of Dunning. All calculations in this study are carried out using the Gaussian 98 quantum chemistry software package.[23]

Results and Discussion

Ten cage isomers of N_{14} are shown in Figures 1–10. Relative energies of these molecules are shown in Table 1. General trends

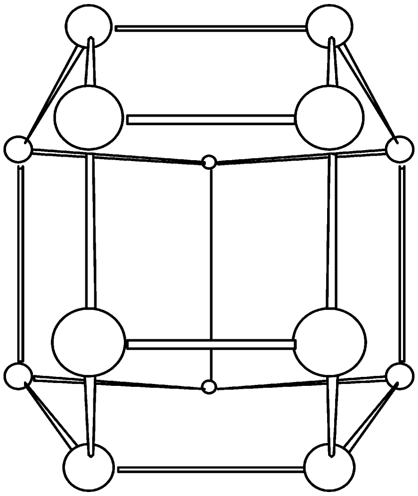

Figure 8. N_{14} isomer 0522 (C_{2v} point group symmetry).

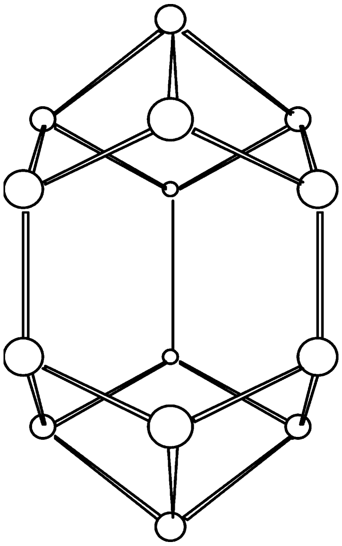

Figure 9. N_{14} isomer 0603 (D_{3h} point group symmetry).

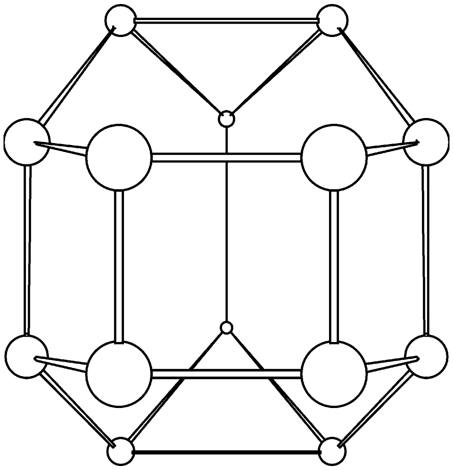

Figure 10. N_{14} isomer 2304 (C_{2v} point group symmetry).

TABLE 1: Relative Energies (in kcal/mol) for Cage Isomers of N_{14} (calculations with cc-pVDZ basis set)

	HF	B3LYP	MP4//HF	MP4//B3LYP
0360	0.0	0.0	0.0	0.0
1251	−4.8	−1.9	−5.5	−6.0
2223	−5.2	−1.4	−9.1	−10.1
2142	+8.3	*a*	+3.5	*a*
3033	+19.9	+15.6	+15.5	+12.6
0441	+34.6	+36.2	+34.7	+34.5
1332	+40.7	*a*	+37.6	*a*
0522	+71.2	+67.7	+69.3	+69.5
0603	+78.9	+78.5	+76.1	+74.2
2304	+87.2	*a*	+81.5	*a*

[a] Geometry optimization failed.

TABLE 2: Relative Energies of N_{14} Cage Isomers with cc-pVDZ and cc-pVTZ Basis Sets (energies in kcal/mol)

	HF/DZ	HF/TZ	B3LYP/DZ	B3LYP/TZ
0360	0.0	0.0	0.0	0.0
1251	−4.8	−4.5	−1.9	−1.9
2223	−5.2	−4.6	−1.4	−1.5
2142	+8.3	+8.9	*a*	*a*
3033	+19.9	+21.5	+15.6	+16.1
0441	+34.6	+34.2	+36.2	+35.8
1332	+40.7	+40.7	*a*	*a*
0522	+71.2	+70.4	+67.7	+66.9
0603	+78.9	+78.0	+78.5	+77.6
2304	+87.2	+87.4	*a*	*a*

[a] Geometry optimization failed.

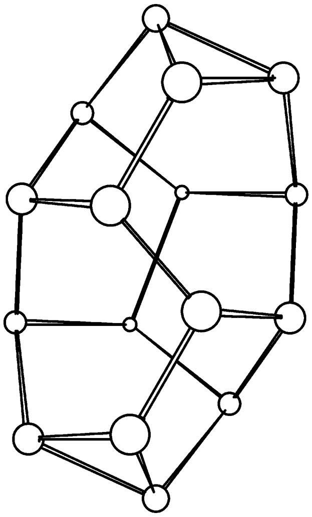

Figure 11. N_{16} isomer 2062 (C_2 point group symmetry).

are evident that correspond to previous studies of N_{12} and N_{18}. For example, higher numbers of pentagons (n_5) yield more stable molecules, as the 0360, 1251, and 2142 isomers are among the most stable. (The stability of the 2223 isomer is exceptional and will be addressed later.) Also, between two isomers of equal n_5, the one with the most triangles (n_3) is generally the most stable, as seen by comparing 2142 versus 0441, 2223 versus 0522, and 3033 versus 1332. One difference between N_{14} and the multiples of six from previous studies is the lack of a single dominant isomer for N_{14}. For N_{12}, the 2060 isomer is clearly most stable, and the 2063 isomer is easily the most stable for N_{18}. However, for N_{14} the four most stable isomers all have energies within 13 kcal/mol of each other, and the two most stable are within four kcal/mol of each other. The inability of N_{14} to form the highly symmetric cages as in the previous studies, along with the triangle−pentagon substructures that stabilize N_{12}, N_{18}, N_{24}, etc., leads to the lack of a single energetically dominant isomer. Table 2 shows that basis set effects are not substantial for N_{14}, as HF and B3LYP energy results with the larger cc-pVTZ basis set do not appreciably differ from the cc-pVDZ results.

The 12 N_{16} cages under consideration in this study are shown in Figures 11−19. Relative energies of these cages are shown in Table 3. Unlike the N_{14} cages, the N_{16} cages have a single

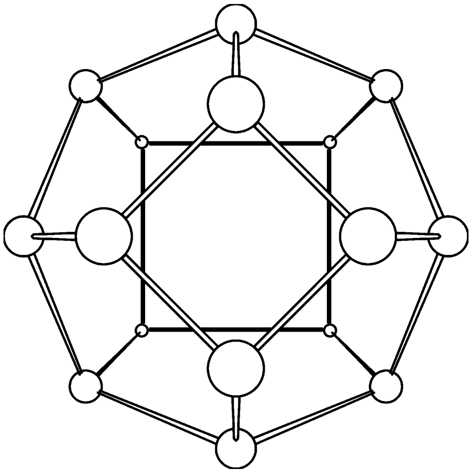

Figure 12. N_{16} isomer 0280 (D_{4h} point group symmetry).

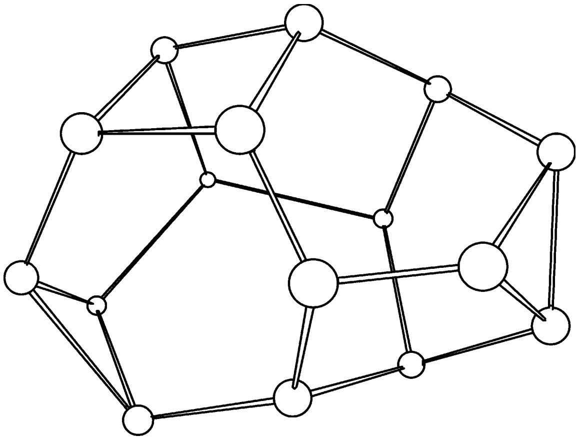

Figure 13. N_{16} isomer 2143 (C_1 point group symmetry).

TABLE 3: Relative Energies (in kcal/mol) for Cage Isomers of N_{16} (calculations with cc-pVDZ basis set)

	HF	B3LYP	MP4//HF	MP4//B3LYP
2062	0.0	0.0	0.0	0.0
0280	+17.0	+17.3	+21.4	+21.7
2143	+40.9	+34.6	+38.6	+38.8
2224A	+41.2	+38.9	+36.7	+36.4
2224B	+49.8	+48.2	+45.9	+45.5
1252A	+50.6	*a*	+51.7	*a*
1252B	+54.1	*a*	+53.0	*a*
0361	+54.3	*a*	+57.1	*a*
1333	+93.3	*a*	+92.7	*a*
4006A	+117.6	+97.4	+108.9	+105.8
4006B	+122.3	+101.8	+112.1	+109.2
0604	+135.2	+126.3	+135.9	+135.3

[a] Geometry optimization failed.

dominant isomer, namely, the 2062 isomer. At the MP4 level of theory, every cage isomer is at least 20 kcal/mol less stable than the 2062 isomer. The 2062 isomer of N_{16} is very much like the 2063 isomer of N_{18} in this regard. Although the N_{16} does not have the highly symmetric substructure in which each triangle is surrounded by three pentagons, the N_{16} 2062 isomer does have two pentagons around each triangle, which is less advantageous than three but still stabilizing. The N_{16} 2062 isomer also has an elongated, roughly cylindrical structure that has also been shown to be energetically favorable. Since 0280 isomer is the second most stable, the N_{16} is also showing the pentagon-favoring general trend seen for N_{14} and previously studied nitrogen cages. However, N_{16} has a pair of isomers, 2224A and 2224B, that seem to have exceptional stability despite a small number of pentagons.

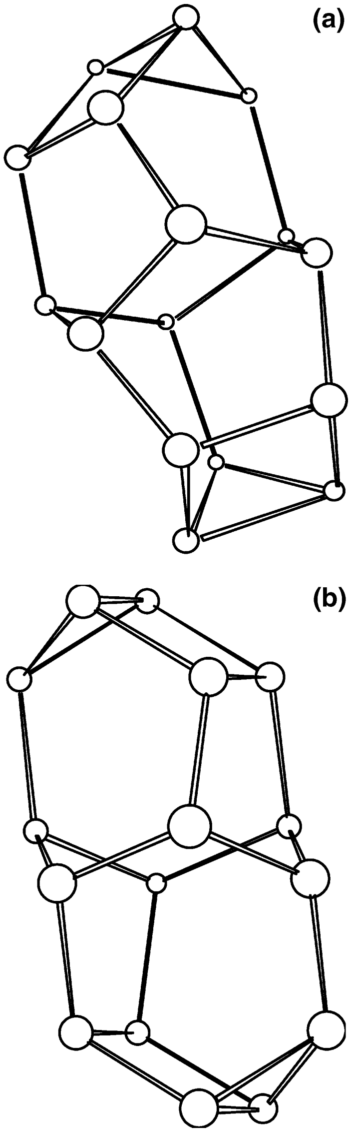

Figure 14. (a) N_{16} isomer 2224A (C_2 point group symmetry). (b) N_{16} isomer 2224B (C_{2h} point group symmetry).

TABLE 4: For Each N_{14} or N_{16} Cage, the Maximum Distance (MaxR) from the Center of Mass of the Cage to an Atom in the Cage (based on HF/cc-pVDZ geometries, distances in angstroms)

N_{14} cages		N_{16} cages	
cage name	MaxR	cage name	MaxR
0360	1.74	2062	2.37
1251	2.07	0280	1.92
2223	2.39	2143	2.27
2142	2.11	2224A	2.50
3033	1.91	2224B	2.52
0441	1.94	1252A	2.13
1332	1.97	1252B	2.14
0522	1.92	0361	1.90
0603	2.17	1333	2.04
2304	1.92	4006A	1.95
		4006B	2.19
		0604	2.07

How can the apparent exceptional stability of N_{14} 2223 and N_{16} 2224A/2224B be understood? Previous studies of nitrogen cages have demonstrated the stability of cylindrical structures over spherical ones due to the favorability of structures that

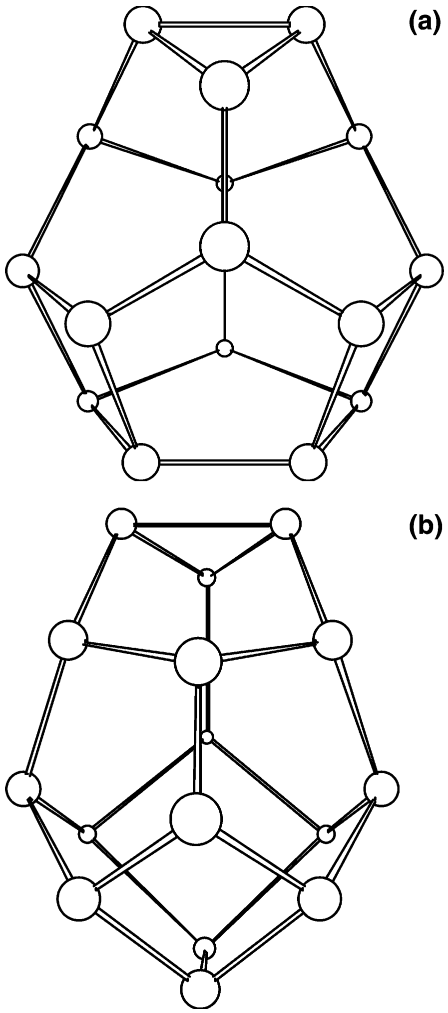

Figure 15. (a) N_{16} isomer 1252A (C_s point group symmetry). (b) N_{16} isomer 1252B (C_s point group symmetry).

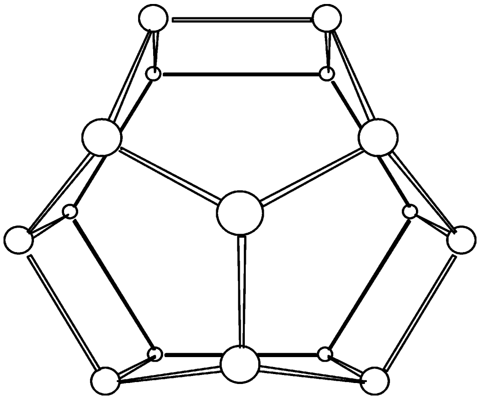

Figure 16. N_{16} isomer 0361 (C_{3v} point group symmetry).

permit pyramidalization of three-coordinate nitrogen. For each cage in this study (N_{14} and N_{16}) Table 4 shows the distance from the center of mass of the molecule to the atom that is farthest from the center of mass. This "maximum radius" (denoted MaxR in Table 4) gives a qualitative measure of the structure of the molecule to distinguish spherical molecules from elongated ones. The HF/cc-pVDZ geometries are used to calculate MaxR. A roughly spherical molecule would have the smallest MaxR because all of the atoms are more or less the same distance from the molecule's center. The most elongated molecules have the largest MaxR values. Table 4 shows that the exceptional molecules 2223, 2224A, and 2224B are the longest molecules in this study for their respective molecule sizes. Therefore, the strain of the triangles and squares in these molecules is most likely being offset by advantageous pyramidalization of the nitrogen atoms. This explains the stability of 2223, 2224A, and 2224B despite the apparent contradiction of previously established trends.

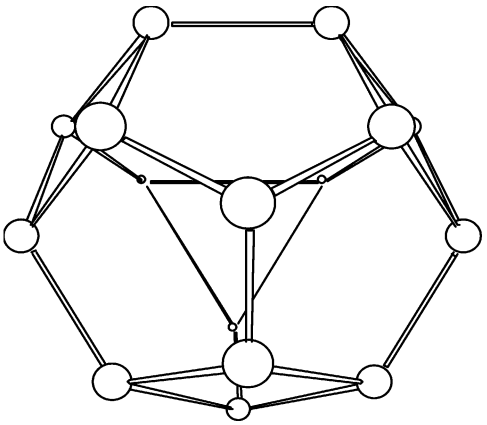

Figure 17. N_{16} isomer 1333 (C_{3v} point group symmetry).

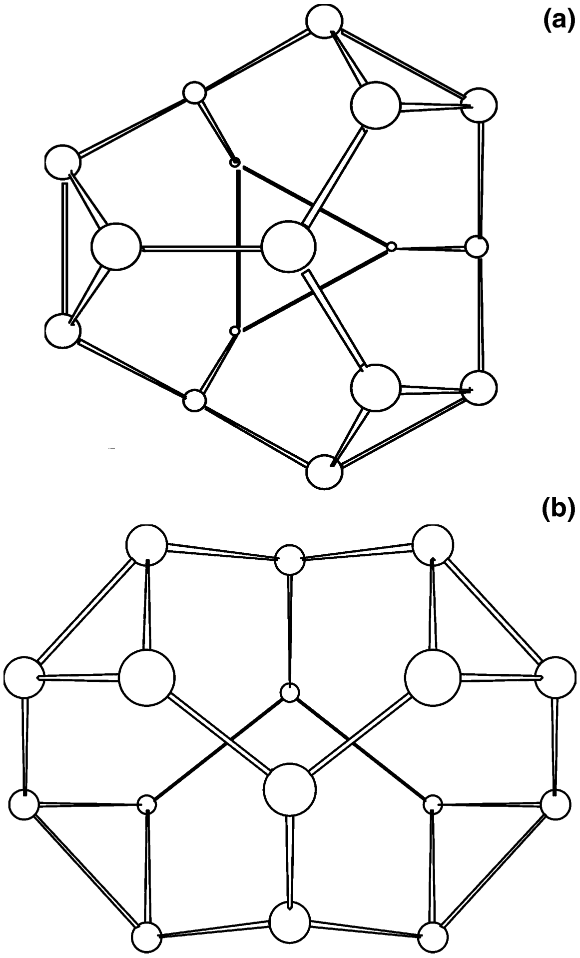

Figure 18. (a) N_{16} isomer 4006A (T_d point group symmetry). (b) N_{16} isomer 4006B (D_{2h} point group symmetry).

Conclusion

Despite the inability to form the highly symmetric structures that are available when the number of atoms is a multiple of six, N_{14} and N_{16} generally follow established trends for cages of three-coordinate nitrogen atoms. At these molecule sizes

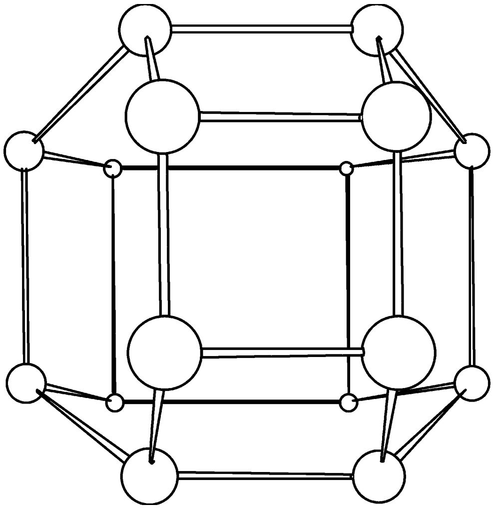

Figure 19. N_{16} isomer 0604 (D_{2h} point group symmetry).

pentagons are still the dominant stabilizing features, with a secondary stabilizing effect from the triangles when the number of pentagons is equal between two isomers. N_{14} shows unique behavior in that several stable isomers are very close in energy. The behavior of N_{16} is closer to that of N_{18} because of structural similarities in the most stable isomer at each molecule size. In general, it is likely that the trends that apply when the number of atoms is a multiple of six also apply otherwise, with unique exceptions that vary with the size of the molecules.

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References and Notes

(1) Fau, S.; Bartlett, R. J. *J. Phys. Chem. A* **2001**, *105*, 4096.

(2) Tian, A.; Ding, F.; Zhang, L.; Xie, Y.; Schaefer, H. F., III *J. Phys. Chem. A* **1997**, *101*, 1946.

(3) Chung, G.; Schmidt, M. W.; Gordon, M. S. *J. Phys. Chem. A* **2000**, *104*, 5647.

(4) Strout, D. L. *J. Phys. Chem. A* **2002**, *106*, 816.

(5) Thompson, M. D.; Bledson, T. M.; Strout, D. L. *J. Phys. Chem. A* **2002**, *106*, 6880.

(6) Li, Q. S.; Liu, Y. D. *Chem. Phys. Lett.* **2002**, *353*, 204. Li, Q. S.; Qu, H.; Zhu, H. S. *Chin. Sci. Bull.* **1996**, *41*, 1184.

(7) Li, Q. S.; Zhao, J. F. *J. Phys. Chem. A* **2002**, *106*, 5367. Qu, H.; Li, Q. S.; Zhu, H. S. *Chin. Sci. Bull.* **1997**, *42*, 462.

(8) Gagliardi, L.; Evangelisti, S.; Widmark, P. O.; Roos, B. O. *Theor. Chem. Acc.* **1997**, *97*, 136.

(9) Gagliardi, L.; Evangelisti, S.; Bernhardsson, A.; Lindh, R.; Roos, B. O. *Int. J. Quantum Chem.* **2000**, *77*, 311.

(10) Schmidt, M. W.; Gordon, M. S.; Boatz, J. A. *Int. J. Quantum Chem.* **2000**, *76*, 434.

(11) Christe, K. O.; Wilson, W. W.; Sheehy, J. A.; Boatz, J. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2004.

(12) Vij, A.; Pavlovich, J. G.; Wilson, W. W.; Vij, V.; Christe, K. O. *Angew. Chem., Int. Ed.* **2002**, *41*, 3051. Butler, R. N.; Stephens, J. C.; Burke, L. A. *Chem. Commun.* **2003**, *8*, 1016.

(13) Fau, S.; Bartlett, R. J. *J. Phys. Chem. A* **2001**, *105*, 4096.

(14) Fau, S.; Wilson, K. J.; Bartlett, R. J. *J. Phys. Chem. A* **2002**, *106*, 4639.

(15) Glukhovtsev, M. N.; Jiao, H.; Schleyer, P. v. R. *Inorg. Chem.* **1996**, *35*, 7124.

(16) Bruney, L. Y.; Bledson, T. M.; Strout, D. L. *Inorg. Chem.* **2003**, *42*, 8117.

(17) Strout, D. L. *J. Phys. Chem. A* **2004**, *108*, 2555.

(18) Sturdivant, S. E.; Nelson, F. A.; Strout, D. L. *J. Phys. Chem. A* **2004**, *108*, 7087.

(19) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(20) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(21) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(22) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.