Why Isn't the N_{20} Dodecahedron Ideal for Three-Coordinate Nitrogen?

Douglas L. Strout*

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

Received: October 13, 2004; In Final Form: December 9, 2004

Nitrogen molecules are the focus of much attention for their potential as high-energy density materials. The usefulness of such molecules as energy sources depends on the stability of the molecules with respect to dissociation. Many such molecules dissociate too easily to be a stable fuel, and the reasons for such instability are related to the details of structure and bonding of the molecule. Such details will be examined for isomers of the molecule N_{20}. N_{20} has a highly symmetric isomer in which the 20 atoms occupy the vertexes of a dodecahedron. This isomer is a cage molecule in which all of the faces are regular pentagons that have interior angles of 108°. These angles are very close to the known bond angles in very stable nitrogen compounds such as ammonia. Such a structure with only pentagons should provide an ideal bonding environment for three-coordinate nitrogen. However, by use of theoretical calculations including density-functional theory and fourth-order perturbation theory, along with the Dunning correlation-consistent basis sets, it will be shown that dodecahedral N_{20} is not the most stable cage for N_{20}. The reasons why will be discussed in terms of the structure and bonding of the molecules.

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 HEDMs, including cyclic and acyclic isomers with 8−12 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. More recently, a network polymer of nitrogen has been produced[13] under very high pressure conditions. Experimental successes have sparked theoretical studies[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 heteroatoms and polyazido isomers[18] 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[19] 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[20] 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[21] 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[22,23] of intermediate-sized molecules N_{14}, N_{16}, and N_{18} 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.

Do these trends apply to N_{20}, which has a spheroidal isomer that is a perfect dodecahedron? The dodecahedron has faces that are regular pentagons, which have internal angles of 108°, very close to the angles seen in well-known stable nitrogen molecules such as ammonia, in which all bonds are single bonds. Ammonia has H−N−H angles of 107.3°.[24] The N_{20} dodecahedron, therefore, is a network of nitrogen atoms that all have a bonding environment that is in some sense ideal. However, this molecule is only one isomer that satisfies the mathematical requirements for an N_{20} cage. If n_3, n_4, n_5, and n_6 are used to represent the number of triangles, squares, pentagons, and hexagons, respectively, then the following bounds exists for a cage isomer of N_{20}

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

$$n_3 + n_4 + n_5 + n_6 = 12$$
$$\text{(because the molecule has 20 atoms)} \quad (2)$$

In the current study, calculations are carried out on N_{20} cage isomers to determine whether this seemingly ideal bonding environment in the dodecahedron does, in fact, make this isomer more stable than other N_{20} cages.

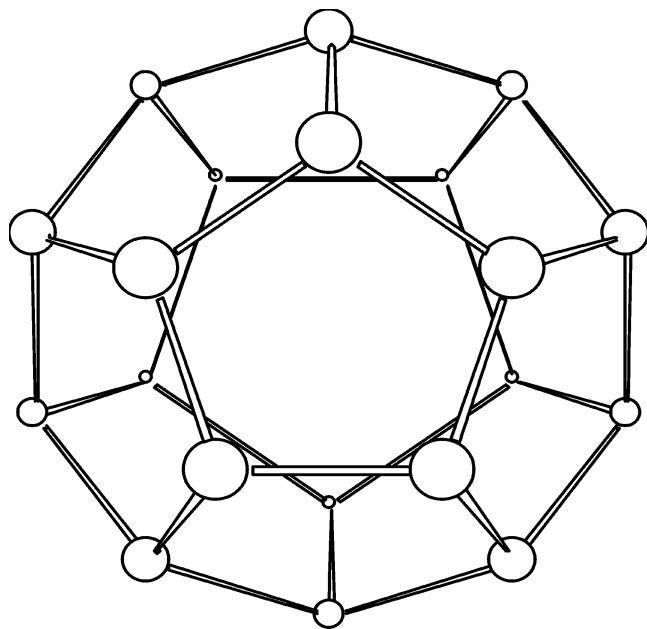* To whom correspondence may be addressed. E-mail: dstrout@alasu.edu.

Ideal Dodecahedron

J. Phys. Chem. A, Vol. 109, No. 7, 2005 **1479**

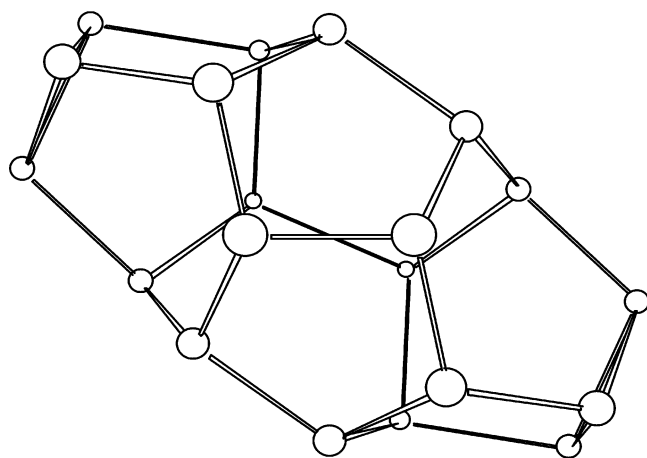**Figure 1.** N_{20} dodecahedron 00(12)0 (I_h point-group symmetry).

Figure 2. N_{20} isomer 2064 (C_2 point-group symmetry).

Computational Methods

Geometry optimizations are carried out with Hartree−Fock theory and the B3LYP density-functional method.[25,26] Single-energy points are calculated with fourth-order perturbation theory[27] (MP4(SDQ)). The basis sets are the correlation-consistent double-ζ (cc-pVDZ), augmented double-ζ (aug-cc-pVDZ), and triple-ζ (cc-pVTZ) sets of Dunning.[28] All calculations in this study have been carried out using the Gaussian03 computational chemistry software package.[29]

Results and Discussion

The N_{20} dodecahedron is shown in Figure 1. This is the so-called "00(12)0" isomer of N_{20} (0 triangles, 0 squares, 12 pentagons, and 0 hexagons). The molecule has I_h point-group symmetry, and all 12 faces are planar five-membered rings with internal bond angles of exactly 108°. This isomer is energetically compared to an isomer that is somewhat structurally similar to the cylindrical N_{18} and N_{24} isomers from previous studies. This isomer, shown in Figure 2, is designated 2064 under the $n_3n_4n_5n_6$ numbering system and lacks the 3-fold symmetry of the N_{18} and N_{24} cylindrical molecules. It does have C_2 point-group symmetry, and it has the triangle on each end, just as the most stable N_{18} and N_{24} molecules do. The difference is that each

TABLE 1: Relative Energies for N_{20} Isomers 00(12)0 and 2064 (Energies in kcal/mol)[a]

energy	geometry	00(12)0 (dodecahedron)	2064 (C_2 symmetry)
HF/DZ	HF/DZ	0.0	−16.1
B3LYP/DZ	B3LYP/DZ	0.0	−19.6
B3LYP/aug-DZ	B3LYP/aug-DZ	0.0	−17.6
B3LYP/TZ	B3LYP/TZ	0.0	−18.7
MP4/DZ	HF/DZ	0.0	−25.7
MP4/DZ	B3LYP/DZ	0.0	−22.7
MP4/aug-DZ	B3LYP/aug-DZ	0.0	−22.0

[a] Basis sets are the cc-pVDZ, aug-cc-pVDZ, and cc-pVTZ sets of Dunning.

TABLE 2: Energies of Rotation around the N−N Bond of Hydrazine (N_2H_4)

rotation angle	B3LYP/cc-pVDZ	B3LYP/aug-cc-pVDZ
0° (eclipsed)[a]	0.00	0.00
5°	−0.07	−0.07
10°	−0.28	−0.26
15°	−0.62	−0.59
20°	−1.08	−1.02

[a] Zero degrees refers to the eclipsed conformation, and other angle measures are rotations from the eclipsed conformation. Energies are in kcal/mol relative to the energy of the eclipsed conformation.

triangle in N_{20} 2064 is surrounded by two pentagons and a hexagon, as opposed to three pentagons in N_{18} and N_{24}. The structural similarities between N_{20} 2064 and the stable isomers at other molecule sizes make the 2064 a good choice for comparison to the 00(12)0 dodecahedron.

Relative energies between the 00(12)0 dodecahedron and the 2064 isomer are shown in Table 1. The data show an across-the-board energetic advantage for the more cylindrically shaped 2064 isomer. (Basis set effects are limited to 1−2 kcal/mol.) This result for N_{20} is in agreement with the preference for cylindrical isomers shown in previous studies, but it seems to defy the advantages the N_{20} dodecahedron should have structurally. The 108° angles that predominate on the dodecahedron should provide a virtually strain-free bonding environment, as opposed to the triangles in the 2064 isomer.

How can the energetic disadvantage on the part of a seemingly ideal isomer be explained? One characteristic of the regular pentagons in the N_{20} dodecahedron is that the dihedral angles between any four consecutive atoms in the same pentagon are always zero. Simply put, the pentagons are planar. From the point of view of any two nitrogen atoms bonded to each other, the two atoms' other bond partners are always in a perfectly eclipsed conformation. Consequently, any two bonded atoms will also have their lone pairs in perfect eclipse as well. This is an energetically unfavorable interaction that is cumulative over the spherical surface of the molecule, resulting in an energetic penalty relative to the 2064 isomer, whose polygons are generally not planar. An estimate of the energy penalty of eclipsing is shown in Table 2. By use of hydrazine as a model, relative energies are calculated between the eclipsed conformation of N_2H_4 and dihedral rotations away from perfect eclipsing. Small angle rotations result in very small energy changes, but the energies change rapidly, up to about 1 kcal/mol at 20°. The 2064 isomer has some intrapolygon dihedral angles up to 20−30° (or more), so the 2064 isomer does not pay the eclipsing penalty like the N_{20} dodecahedron does. Over the surface of a 20-atom spheroid, the cumulative eclipsing penalty is substantial enough that the 2064 isomer is more stable despite the 60° bond angles in the triangles.

Conclusion

Despite an apparently ideal structural environment, the N_{20} dodecahedron is not the most stable cage isomer. The cause is an energetic penalty resulting from the eclipsed atoms and lone pairs in the planar pentagons in the N_{20} dodecahedron. A more cylindrically shaped isomer (the 2064) is more stable than the dodecahedron because its nonplanar polygons do not incur this penalty. Other isomers beside 2064 may be more stable than the dodecahedron for the same reason. Also, this eclipsing effect may contribute to the instability of spheroidal isomers relative to cylindrical ones at other molecule sizes as well.

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) Eremets, M. I.; Gavriliuk, A. G.; Trojan, I. A.; Dzivenko, D. A.; Boehler, R. *Nature Mater.* **2004**, *3*, 558.

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

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

(16) Knapp, C.; Passmore, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 4834.

(17) Haiges, R.; Schneider, S.; Schroer, T.; Christe, K. O. *Angew. Chem., Int. Ed.* **2004**, *43*, 4919.

(18) Huynh, M. V.; Hiskey, M. A.; Hartline, E. L.; Montoya, D. P.; Gilardi, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 4924.

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

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

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

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

(23) Strout, D. L. *J. Phys. Chem. A* **2004**, *108*, 10911.

(24) Chang, R. *Chemistry*, 8th ed.; McGraw-Hill: New York, 2005.

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

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

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

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

(29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision B.01; Gaussian, Inc.: Pittsburgh, PA, 2003.