RESEARCH ARTICLE

The Shape of Three-Coordinate Nitrogen Cages

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Abstract

Complex forms of nitrogen are of scientific interest for their energetic properties. A number of different forms of nitrogen have been the subject of experiment and/or theoretical studies. One such form is the three-coordinate cage, some of which are a nitrogen-based analogue to the well-known carbon fullerenes. Such cages N_x would decompose by $N_x \rightarrow (x/2)\ N_2$, with the release of substantial amounts of energy. A study of N_{20} cages, one of which is the analogue of the smallest fullerene C_{20}, revealed that the pentagon-hexagon network favored by carbon is NOT favored by nitrogen. Other cages, based on other polygons, are more thermodynamically stable for nitrogen. In this review, multiple studies of the properties of nitrogen cages are considered and trends regarding structure and energy are discussed.

Introduction

High-energy nitrogen has been the subject of numerous scientific studies, experimental and theoretical, because of the high exothermicity of reactions of the type $N_x \rightarrow (x/2)\ N_2$. While molecular N_2 and the azide N_3^- ion have been well known for many years, more recent experimentally-verified nitrogen forms include the N_5^+ and N_5^- ions[1–3], as well as the N_7O^+ and CN_7^- ions[4–5], various azido compounds[6–9], and a network polymer of nitrogen[10]. A class of molecules that have received much theoretical attention is the nitrogen cage[11–17]. A nitrogen cage is a closed three-dimensional structure composed of polygons in a manner similar to carbon fullerenes. Any cage of three-coordinate atoms (whether carbon or nitrogen) will have a network of polygons subject to Euler's Theorem,

$$\Sigma\ n_i\ (6 - i) = 12$$

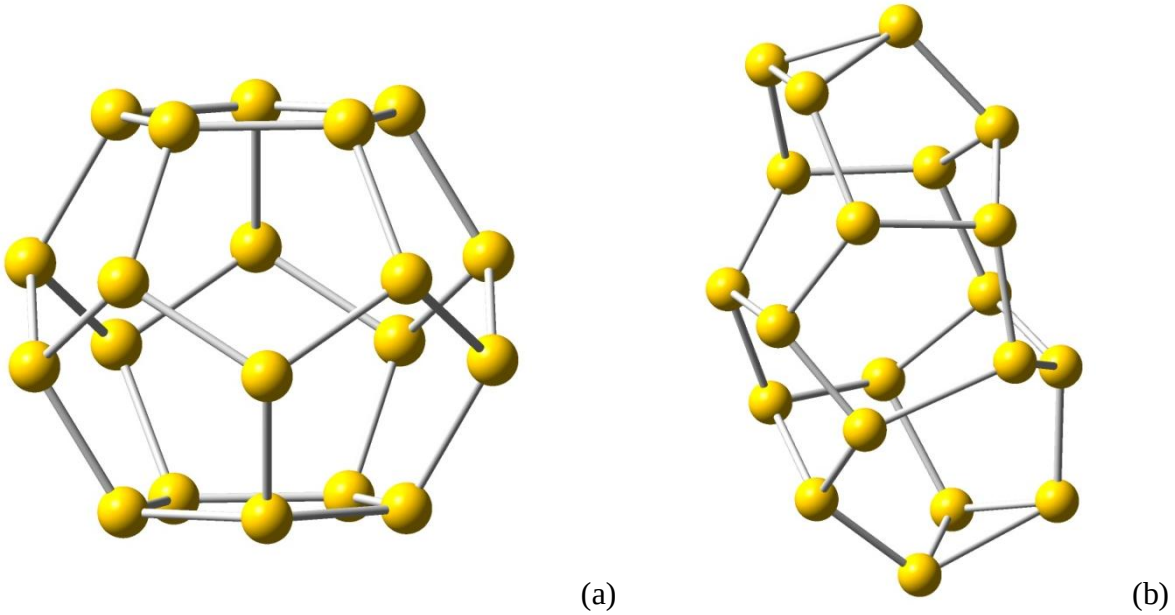
where n_i is the number of i-sided polygons in the cage. If the assumption is made that the network is limited to triangles, squares, pentagons, and hexagons, then Euler's Theorem reduces to

$$3n_3 + 2n_4 + n_5 = 12$$

where n_3 is the number of triangles, n_4 is the number of squares and n_5 is the number of pentagons.

The differences in bonding between carbon and nitrogen lead to major differences in the

structure of cage molecules. Three-coordinate carbon has sp^2 hybridization, and the bonding is that of benzene or graphite, favoring planar structures. Three-coordinate nitrogen has sp^3 hybridization and favors the pyramidal bonding found in compounds such as ammonia and hydrazine. This difference has been explored in a computational study[18] on isomers of N_{20}. A dodecahedron-shaped N_{20}, analogous to the smallest carbon fullerene C_{20}, was compared to a more-cylindrical, less-symmetric isomer. These molecules are shown in Figure 1. The dodecahedron is actually the LESS stable isomer, because the high symmetry causes eclipsing of the nitrogen lone pairs (the N_{20} study showed that staggering the lone pairs by even 20^o confers more than 4 kJ/mole stability per N-N bond). Additionally, the spheroidal structure of the fullerene-like N_{20} has the flattest possible cage curvature, which is FAVORABLE for graphitic carbon but UNFAVORABLE for pyramidal nitrogen. Is the N_{20} study a single point in a larger trend? Do nitrogen cages and carbon cages really have such widely divergent structures?



(a) (b)

Figure 1. Cage isomers of N_{20}: (a) spherical fullerene-like pentagon-hexagon isomer, (b) cylindrical isomer with triangular end-caps.

Computational Methods

Computational studies described in this review have used a variety of computational methods, including density functional theory[19,20] (B3LYP and PBE1PBE), Moller-Plesset perturbation theory[21], and coupled-cluster theory[22]. The Dunning correlation-consistent atomic orbital basis sets[23] have been used in all studies described in this review. Calculations in the various studies have been performed using the Gaussian computational chemistry software[24] and its Windows counterpart GaussianW.

Results and Discussion

N_{20}. In the N_{20} study[18], cages are described by numerical labels $n_3n_4n_5n_6$, where n_3, n_4, n_5, and n_6 represent the number of triangles, squares, pentagons, and hexagons, respectively, in each cage. For example, the N_{20} cage analogue to the fullerene C_{20} is designated 00(12)0 because it has 12

pentagons and none of the other polygons. That molecule has icosahedral I_h symmetry and perfect eclipsing of atoms and lone pairs around each of the nitrogen-nitrogen single bonds. The comparison molecule is closer to cylindrical in shape and is designated 2064 (two triangles, zero squares, six pentagons and four hexagons). The 2064 molecule has only C_2 symmetry, a much less spherical shape, and more staggering of atoms and lone pairs around the N-N bonds. Both molecules are shown in Figure 1, and the relative energies of the two molecules are shown in Table 1.

TABLE 1. Relative energies of the fullerene-like (00(12)0) and cylindrical (2064) isomers of N_{20}. Energies in kJ/mole. B3LYP refers to density functional theory, and MP4 refers to fourth-order Moller-Plesset perturbation theory.

Method	Basis set	Fullerene (00(12)0)	Cylinder (2064)
B3LYP	cc-pVDZ	0.0	−82.0
B3LYP	aug-cc-pVDZ	0.0	−73.6
B3LYP	cc-pVTZ	0.0	−78.2
MP4	cc-pVDZ	0.0	−95.0
MP4	aug-cc-pVDZ	0.0	−92.0

The data in Table 1 show that B3LYP predicts that the more cylindrical isomer is more stable by about 70−80 kJ/mole, whereas MP4 favors the cylindrical isomer by 90−95 kJ/mole. In the N_{20} study, this was explained as an effect related to the eclipsing of nitrogen lone pairs. The fullerene-shaped N_{20} has icosahedral symmetry with perfect eclipsing of all nitrogen-nitrogen bonds, whereas the cylindrical 2064 isomer is more irregular and has more staggering of the nitrogen-nitrogen bonds. Using hydrazine as a model molecule, it was shown that even a 20° rotation of a nitrogen-nitrogen bond away from the eclipsed conformation results in more than 4 kJ/mole of stabilization. The energy differences in Table 1 can be viewed as the cumulative effect of the staggering of bonds over the surface of the 2064 cage.

Larger cages: Spheres vs Cylinders. A separate study[17] on N_{24}, N_{30}, and N_{36} compared spherical, fullerene-like cages with more cylindrical structures. Example structures are shown in Figure 2. The spherical cages are modeled after their pentagon-hexagon carbon counterparts, and the cylindrical cages are end-capped with triangles surrounded by pentagons, with hexagons making up the balance of the cylinder's length. The results show a progressive trend in which the energetic favoring of the cylinder increases with increasing molecule size. For N_{24} and N_{30}, Table 2 shows that the cylinder is favored much more than it is for N_{20} (compare Table 2 with Table 1). Table 2 also shows that the favoring of the cylinder increases even more for N_{36}. The effect is one of fundamental difference in shape; as a spheroid's radius increases, its surface curvature decreases. While such flattening is favorable for carbon, it is unfavorable for nitrogen. This trend is shown in the data in Table 2.

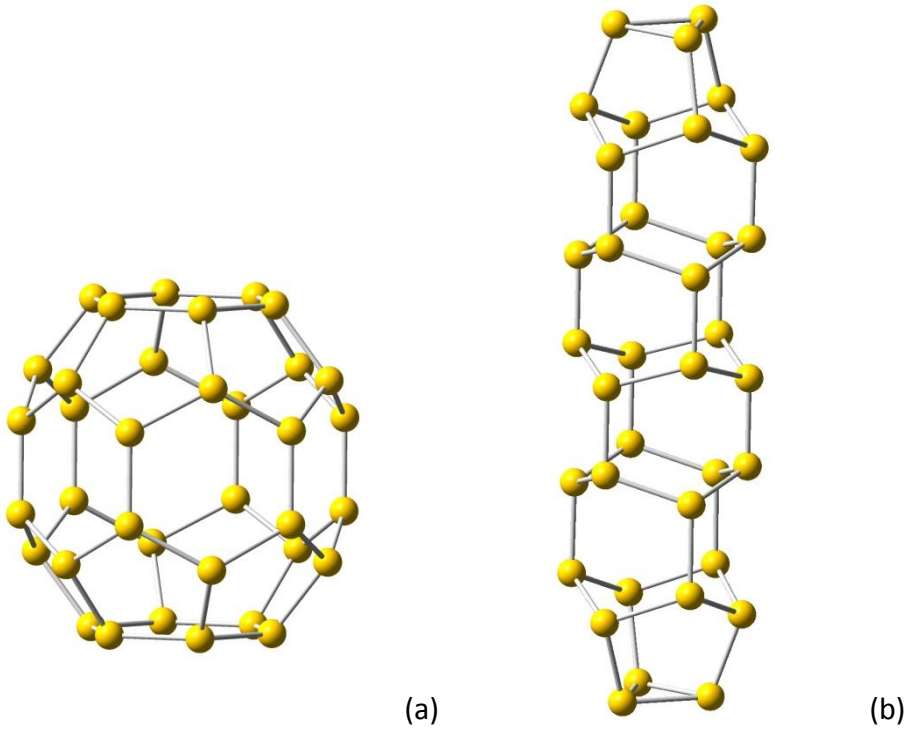
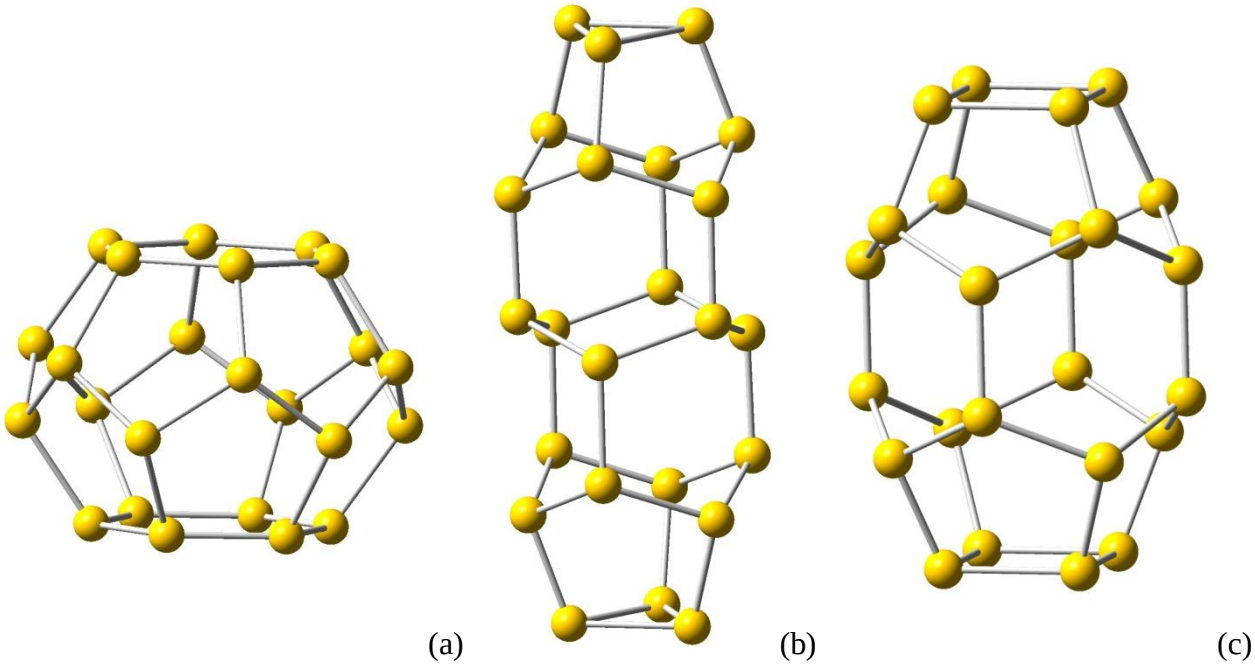


Figure 2. Cage isomers of N_{36}: (a) fullerene-like isomer, (b) cylindrical isomer.

TABLE 2. Relative energies of cylindrical isomers of N_{24}, N_{30}, and N_{36} compared with their fullerene-like counterparts. Energies in kJ/mole. Negative values indicate that the cylindrical isomer is more stable than the corresponding fullerene-like molecule.

Method	Basis set	N_{24}	N_{30}	N_{36}
B3LYP	cc-pVDZ	−340.6	−336.8	−1326.3
B3LYP	cc-pVTZ	−325.1		
MP4	cc-pVDZ	−448.9	−384.1	−1588.7

Mixed carbon-nitrogen cages. If carbon cages favor the spherical pentagon-hexagon shape, and nitrogen cages favor cylindrical cages, what about molecules with mixed content including both carbon and nitrogen atoms? A pair of studies[25,26] of the N_{24} cages has been carried out to include progressive carbon substitution, resulting in molecules $N_{22}C_2$, $N_{20}C_4$, and so forth. Three structures are considered in these studies: A cylindrical structure with end-cap triangles, a cylindrical structure with end-cap squares, and a fullerene-like structure with pentagons and hexagons. Each structure is shown in Figure 3. The goal of the study is to determine the degree of carbon substitution required for fullerene-like cages to become the energetically favored structure. Carbon atoms are substituted into the structure in pairs to allow carbon-carbon double bonding to satisfy the fourth valence of each carbon atom. Table 3 shows the relative energies of the three structures as a function of increasing carbon substitution.



(a) (b) (c)

Figure 3. Cage isomers of N_{24} considered for the mixed carbon-nitrogen study: (a) fullerene-like isomer (carbon atoms were substituted pairwise into the hexagons), (b) cylindrical isomer with triangular end-caps (carbon atoms were substituted pairwise parallel to the long axis of the molecule), (c) cylindrical isomer with square end-caps (carbon atoms were substituted pairwise at the junctions between the hexagons).

TABLE 3. Relative energies of cylindrical isomers of $N_{22}C_2$, $N_{20}C_4$, $N_{18}C_6$, and $N_{16}C_8$. Energies in kJ/mole. Negative values indicate greater stability. "Triangle" refers to the isomer with triangular end-caps. "Square" refers to the isomer with square end-caps. "Fullerene" refers to the pentagon-hexagon isomer. All calculations carried out with Dunning cc-pVDZ atomic orbital basis set.

Formula	Isomer	PBE1PBE	CCSD(T)
$N_{22}C_2$	Triangle	0.0	0.0
	Square	+170.3	+187.9
	Fullerene	+291.2	+307.5
$N_{20}C_4$	Triangle	0.0	0.0
	Square	+58.2	+69.0
	Fullerene	+154.8	+171.1
$N_{18}C_6$	Triangle	0.0	0.0
	Square	−195.4	−165.3
	Fullerene	−137.7	−108.8
$N_{16}C_8$	Square	0.0	0.0
	Fullerene	−25.1	−31.8

For $N_{22}C_2$, the structure with the triangle end-caps is the most stable by more than 170 kJ/mole. However, with two additional carbon atoms ($N_{20}C_4$), the energy gap between the isomers has narrowed substantially, as the "square" and "fullerene" isomers have a flatter curvature that stabilizes the additional sp^2-hybridized carbon atoms. For $N_{18}C_6$, this additional stabilization of the carbon causes the square and fullerene isomers to become more stable than the triangle-based isomer. For this reason, consideration of the "triangle" isomer is discontinued at this point. The only $N_{16}C_8$ isomers considered here are the square and fullerene isomers. Table 3 shows that the fullerene-like $N_{16}C_8$ has the greatest stability. Since C_{24} is a fullerene-shaped cage molecule, it is assumed $N_{14}C_{10}$, $N_{12}C_{12}$, and so on, would also favor a fullerene-like shape.

Conclusions

(1) The differences between carbon and nitrogen as to their bonding characteristics result in very different structures for three-coordinate cages, namely that carbon prefers spherical shapes and nitrogen prefers cylindrical shapes.

(2) Progressive carbon substitution into an otherwise all-nitrogen cage introduces carbon's tendency toward spherical structure, resulting in the spherical fullerene-like structure becoming the favored structure once the carbon content is at least one-third of the molecule.

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