Inorg. Chem. **2003**, *42*, 8117–8120

Inorganic Chemistry Article

What Makes an N_{12} Cage Stable?

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Received June 18, 2003

Much recent attention has been given to molecules containing only nitrogen atoms. Such molecules N_x can undergo the reaction $N_x \rightarrow (x/2)N_2$, which is very exothermic. These molecules are potential candidates for high energy density materials (HEDM). However, many all-nitrogen molecules dissociate too easily to be stable, practical energy sources. It is important to know which nitrogen molecules will be stable and which will not. In the current study, a variety of N_{12} cages with all single bonds are examined by theoretical calculations to determine which ones are the most thermodynamically stable. Calculations are carried out using Hartree–Fock (HF) theory, gradient-corrected density functional theory (DFT), and Moller–Plesset perturbation theory (MP2 and MP4). Relative energies among the various isomers are calculated and trends are examined in order to determine which structural features lead to the most energetically favorable molecules.

Introduction

Molecules consisting entirely of nitrogen atoms have been extensively studied as candidates for high energy density materials (HEDM). A molecule N_x can undergo the reaction $N_x \rightarrow (x/2)N_2$, which is exothermic by more than 50 kcal/mol per nitrogen atom. The difficulty with many such molecules is that they dissociate or isomerize too easily to serve as practical energy sources. It has been suggested[1] that an N_x molecule have barriers to dissociation and isomerization of at least 30 kcal/mol. Many N_x molecules have been shown by theoretical calculations to dissociate with barriers below 30 kcal/mol, including several cyclic and acyclic isomers[1−5] with eight to twelve nitrogen atoms. Cage isomers of N_8 and N_{12} have also been shown[5−8] to dissociate too easily to be HEDM.

Significant advances have also taken place in the experimental synthesis of nitrogen molecules. The recent synthesis[9] of the N_5^+ cation has opened new possibilities for production of all-nitrogen molecules. The production of N_5^+ also led to a theoretical study[10] of N_8 molecules that could be produced by an addition reaction between the N_5^+ ion and the N_3^- azide ion. None of the N_8 products was judged to be stable enough to be a practical HEDM. Also, the N_5^- anion has been experimentally synthesized,[11] and a theoretical study has suggested[12] that an N_5^+/N_5^- ion pair would be stable enough to serve as a useful HEDM. As even larger N_x molecules or ions are produced in the laboratory, the possibilities for synthesis of all-nitrogen HEDM will increase further.

Several theoretical studies have characterized a variety of isomers of N_{12}. Glukhovtsev et al. calculated[13] the stability of diazobispentazole and open-chain isomers of N_{12}. Olah et al. characterized N_{12} isomers derived from the N_6^{2+} dication.[14] Li and Zhao have calculated[5] dissociation barriers for several isomers, including an N_{12} ring and two N_{12} three-coordinate cages. In the current study, a wide variety of N_{12} cages are examined to determine the stability trends and the structural features that lead to more thermodynamically stable

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10.1021/ic034696j CCC: $25.00 © 2003 American Chemical Society

Published on Web 10/24/2003

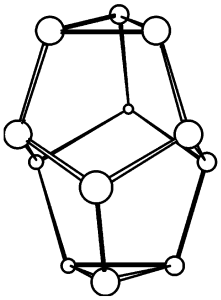

Figure 1. N_{12} isomer 2060 (D_{3d} symmetry).

cage molecules. The cage isomers are composed of three-coordinate nitrogen in a spheroidal network of polygons. The polygons in this study are limited to triangles, squares, pentagons, and hexagons, with the number of polygons of each type represented by n_3, n_4, n_5, and n_6, respectively (the term n_i shall stand for the number of i-sided polygons). The polygons on the surface of each N_{12} cage molecule are subject to the following mathematical bounds:

(a) $3n_3 + 2n_4 + n_5 = 12$ (Euler's Theorem)

(b) $n_3 + n_4 + n_5 + n_6 =$ 8 (because each molecule has 12 atoms)

Computational Details

Geometry optimizations were performed on all isomers at three levels of theory: Hartree–Fock, density functional theory[15,16] (B3LYP), and second-order Moller–Plesset perturbation theory[17] (MP2). Single energy points have been carried out with fourth-order Moller–Plesset perturbation theory (MP4(SDQ)). All calculations were performed using the CC-PVDZ basis set of Dunning.[18] All molecules in this study have singlet electronic ground states. The Gaussian 98 computational chemistry software package[19] was employed for all calculations in this study.

Results and Discussion

Each isomer in this study shall be referred to by a four-digit number $n_3n_4n_5n_6$. Figures 1–9 depict the nine isomers in this study, and these isomers shall be referred to by their polygon counts. For example, the isomer in Figure 1 is designated the 2060 isomer because it has two triangles, no squares, six pentagons, and no hexagons. The relative energies of all nine isomers in this study are shown in Table 1, catalogued by their $n_3n_4n_5n_6$ specifications. (Isomers with specifications 1250, 3032, and 2303 were sought but not found.) The general trend in isomer stability is that cages with more pentagons are more stable, with 2060 having the most pentagons and being the most stable. 4004 and 0602, the two isomers completely without pentagons, are the least stable. This trend is consistent for all six levels of theory shown in Table 1. There is a secondary trend that, for any two isomers with equal numbers of pentagons, the one with more triangles will be more stable. Three pairs of isomers, 2141 and 0440, 3113 and 1412, and 4004 and 0602, all support the secondary trend. All nine N_{12} isomers are

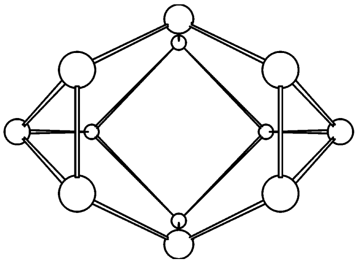

Figure 2. N_{12} isomer 2141 (C_{2v} symmetry).

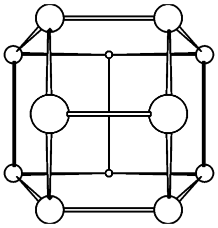

Figure 3. N_{12} isomer 0440 (D_{2d} symmetry).

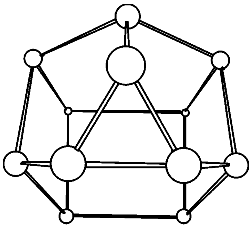

Figure 4. N_{12} isomer 1331 (C_s symmetry).

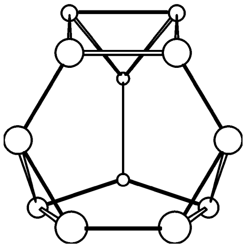

Figure 5. N_{12} isomer 3113 (C_s symmetry).

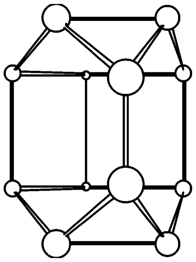

Figure 6. N_{12} isomer 2222 (C_{2v} symmetry).

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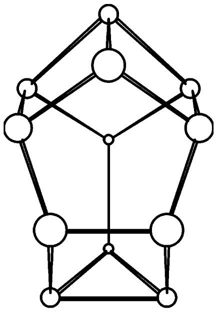

Figure 7. N_{12} isomer 1412 (C_s symmetry).

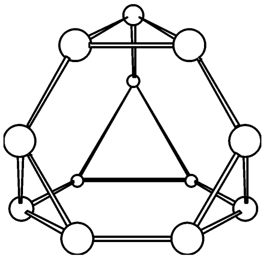

Figure 8. N_{12} isomer 4004 (T_d symmetry formally, but optimized in D_{2d} symmetry).

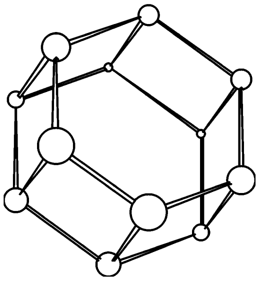

Figure 9. N_{12} isomer 0602 (D_{6h} symmetry).

Table 1. Relative Energies (in kcal/mol) of N_{12} Cage Isomers (Calculations Performed with CC-PVDZ Basis Set)

isomer	HF	B3LYP	MP2	MP4//HF	MP4//B3LYP	MP4//MP2
2060	0.0	0.0	0.0	0.0	0.0	0.0
2141	+32.7	+30.6	+38.9	+32.9	+32.7	+24.2
0440	+49.8	+46.4	+62.7	+51.0	+51.8	+44.1
1331	+64.3	*a*	*a*	+63.2	*a*	*a*
3113	+68.4	*a*	*a*	+63.1	*a*	*a*
2222	+73.9	*a*	*a*	+68.8	*a*	*a*
1412	+81.0	+73.3	+88.2	+78.0	+77.4	+68.4
4004	+95.5	*a*	*a*	+82.9	*a*	*a*
0602	+154.7	+146.5	+172.5	+154.1	+153.3	+143.6

[a] Result unavailable due to geometry optimization failure.

confirmed minima (zero imaginary frequencies) at the HF/CC-PVDZ level of theory (the 4004 isomer was optimized in D_{2d} symmetry even though it formally has T_d symmetry). The five isomers successfully optimized with B3LYP/CC-PVDZ have also been confirmed as minima by B3LYP/CC-PVDZ frequencies.

The energetic favoring of pentagons is straightforward to understand in terms of the behavior of three-coordinate nitrogen. Nitrogen atoms with three single bonds prefer bond angles that are nearly tetrahedral, such as the 107.3° H−N−H angles of NH_3. An ideal regular pentagon has interior angles of 108°, very favorable for three-coordinate nitrogen. The pentagons in the N_{12} molecules are not regular, but they still have favorable bond angles. For example, the pentagons in 2060 have three symmetry-independent angles. At the HF/CC-PVDZ level of theory, these angles are 106.8° (triangle atom as vertex), 104.4° (triangle atom as end), and 103.4° (angle formed by three equatorial atoms). With MP2/CC-PVDZ, these angles are 105.2°, 106.7°, and 101.8°, respectively. Compared with 60° angles from triangles and 90° angles from squares, these pentagonal angles are much more favorable. The 2060 isomer is the most stable because six of the twelve atoms are vertices shared by three pentagons, a nearly ideal bonding environment for nitrogen. (By contrast, the 1331 isomer has one atom in a three-pentagon environment, and none of the others have any.)

Table 2. Bond Lengths for 2060 Isomer for HF/CC-PVDZ, B3LYP/CC-PVDZ, and MP2/CC-PVDZ Geometry Optimizations (Optimizations in D_{3d} Symmetry, Bond Lengths in Å)

bond	HF	B3LYP	MP2
triangle bond	1.443	1.534	1.625
bond radiating from triangle	1.409	1.420	1.386
equatorial bond	1.438	1.493	1.514

The secondary trend favoring triangles can be understood in terms of polygon substitution between triangles and squares. Maintaining a constant number of pentagons, two triangles and a hexagon would be exchanged for three squares. Two triangles have a total of six strained angles, whereas three squares have a total of twelve strained angles, an unfavorable exchange that causes, for example, the 2141 isomer to be more stable than 0440. Furthermore, isomers with large numbers of squares tend to have edge-sharing pairs of squares, which causes some atoms to have two or even three strained 90° angles. Well-distributed triangles are therefore favored over edge-sharing squares.

In order to determine if a low-lying triplet state exists for the 2060 isomer, triplet energy points have been carried out with HF/CC-PVDZ and MP2/CC-PVDZ at the respective singlet optimized geometries for each method. (Because D_{3d} symmetry may yield spatially degenerate triplet wave functions, the energies were calculated in the C_{2h} subgroup.) The results are vertical transition energies of +167.4 kcal/mol with HF theory and +74.4 kcal/mol with MP2. Such large excitation energies indicate that the molecule is well described by a single ground-state configuration, which is supported by the HOMO−LUMO gap of 0.55 hartrees for the 2060 isomer. Since all nine molecules in this study have HOMO−LUMO gaps of 0.5−0.6 hartrees, it is likely that the single-reference methods used in this study give reasonably accurate results.

Several B3LYP and MP2 optimizations were dissociative, that is, the molecule did not survive with all eighteen bonds intact. One or more bonds opened up, resulting in “bond lengths” of 2 Å or more. This is a result of the tendency of B3LYP and MP2 toward longer bond lengths relative to HF. As an example, the bond lengths of the 2060 isomer have been tabulated in Table 2. In D_{3d} symmetry, the molecule only has three symmetry-independent bonds. B3LYP bond lengths are longer than HF lengths, with MP2 bond lengths even longer than the B3LYP results. For other molecules, this lengthening effect results in bond dissociation and a failed optimization. However, the observed trends in this study are not significantly affected by these failures. First, the failures only occurred for molecules that are relatively high in energy. Further, the MP4//B3LYP results closely follow MP4//HF, so it is unlikely that a full set of MP4//B3LYP results would show substantial reversals of isomer energies. The MP4//MP2 energies relative to 2060 are lower compared to MP4//HF and MP4//B3LYP, but this may be due to the severe bond stretches of the 2060 molecule by MP2 theory.

The energy trends in this study follow those in a previous study[20] on cage isomers of N_8. In that study, three N_8 isomers with all N−N single bonds were thermodynamically characterized with respect to each other and with respect to 4 N_2. Using the numbering system in the current study, the three N_8 molecules would be designated 0600 (the N_8 cube with six squares and no other polygons), 4002, and 2220. In the N_8 study, the 2220 molecule has the most pentagons and is lowest in energy, just as the 2060 isomer is lowest for N_{12}. Between the other N_8 molecules, 0600 and 4002, neither of which has any pentagons, 4002 is more stable, which agrees with the N_{12} secondary trend favoring triangles.

Conclusion

Among the N_{12} cages in this study, the isomers with the most pentagons, 2060, 2141, and 0440, have the lowest energies. Conversely, the isomers with no pentagons, 4004 and 0602, are the least stable. The pentagons are the primary structural features that contribute to the stability of the molecules. Triangles in the molecular structure have a secondary stabilizing effect on the N_{12} cages. These trends agree with previous results on the smaller N_8 molecules. Among the various cage isomers, molecules with triangles and pentagons are most likely to show promise as high energy density materials. Whether all-nitrogen cage molecules larger than N_{12} have the same relationships between structure and stability remains an open question.

Acknowledgment. The Alabama Supercomputer Authority is gratefully acknowledged for a grant of computer time on the Cray SV1 in Huntsville, AL. L.Y.B. is an undergraduate scholar supported by the Minority Access to Research Careers (MARC) Program administered by the National Institute of General Medical Sciences (NIH/NIGMS 5T34GM08167-17). D.L.S. is supported by MARC as a faculty research mentor. The taxpayers of the state of Alabama in particular and the United States in general are gratefully acknowledged.

Supporting Information Available: Cartesian coordinates for all nine N_{12} molecules in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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