J. Phys. Chem. A 2005, 109, 8011−8015

Stability of Nitrogen−Oxygen Cages $N_{12}O_2$, $N_{14}O_2$, $N_{14}O_3$, and $N_{16}O_4$

Karleta D. Colvin and Douglas L. Strout*

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

Received: June 27, 2005

Molecules consisting entirely of nitrogen have been studied extensively for their potential as high energy density materials (HEDM). However, many such molecules are too unstable to serve as practical energy sources. This has prompted many studies of molecules that are mostly nitrogen but which incorporate heteroatoms into the structure to provide additional stability. In the current study, cages of three-coordinate nitrogen are viewed as candidates for stabilization by insertion of oxygen atoms into the nitrogen framework. Cages of N_{12}, N_{14}, and N_{16} with four-membered rings are studied because four-membered rings have been previously shown to be a destabilizing influence. Insertion of oxygen atoms, which converts N−N bonds to N−O−N bonding groups, relieves ring strain and can potentially result in stable molecules. These molecules are studied by theoretical calculations, using Hartree−Fock and Moller−Plesset (MP3 and MP4) theories, to determine the dissociation energies of the molecules. The primary result of the study is that stable molecules can result from oxygen insertion but that oxygen−oxygen proximity destabilizes the insertion products.

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 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 introduction of heteroatoms provides a possible solution to the instability of small N_x cages. Previous studies[19−21] of N_x cages ($x = 12−18$) have shown that four-membered rings in the cage structure have a destabilizing influence; cage molecules with four-membered rings are generally less stable than their counterparts. It has been suggested[22] that the insertion of oxygen atoms into the nitrogen network will relieve the strain and lead to more stable structures. Such insertion would replace an N−N single bond with two N−O single bonds. Previous studies[23,24] of oxygenation of the N_8 cubic molecule indicate that there exists an N_8O_6 that may be stable enough to be a useful HEDM, but several isomers of N_8O_4 have been shown to have low-energy paths to dissociation. The number of oxygen atoms is an important factor in determining the degree to which cage strain is relieved. However, since oxygen insertion tends to dilute the per-atom energy delivery of the molecules, oxygenation of all the N−N bonds should be avoided. Instead, for optimal design of an HEDM, only the number of oxygens necessary for stabilization should be inserted.

In the current study, cage isomers of N_{12}, N_{14}, and N_{16} with four-membered rings are considered as candidates for stabilization by oxygen insertion. The inserted oxygen atoms open up the four-membered rings into pentagons and hexagons, thereby relieving ring strain within the structure. Since maximizing nitrogen content is another relevant issue, the nitrogen cages are chosen such that four-membered rings share edges, so that a single inserted oxygen can open up two four-membered rings. This keeps the number of inserted oxygens relatively low, thereby maintaining a high percentage of nitrogen in the molecules. Previous nomenclature[19−21] for nitrogen cages designates them according to the number of triangles, four-membered rings, pentagons, and hexagons in the structure, resulting in a four-digit label $n_3n_4n_5n_6$ for each nitrogen cage. In each case, n_i is the number of i-sided polygons in the molecule. The nitrogen cages chosen for this study are the N_{12} 0440, N_{14} 0441, N_{14} 0522, and N_{16} 0604 isomers. (Note: each of the cages has zero triangles ($n_3 = 0$) and a relatively large value of n_4.) These nitrogen cages are shown in Figures 1−4, respectively. These molecules are subjected to oxygen insertion to relieve ring strain in the four-membered rings, and the stability of the oxygen insertion products is determined to identify which ones may be viable high-energy density materials.

Computational Details

The geometries of each insertion product and its dissociation intermediates are optimized with Hartree−Fock theory and third-order Moller−Plesset theory[25] (MP3). Single-point energies for $N_{12}O_2$ are carried out with fourth-order Moller−Plesset theory

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[*] To whom correspondence should be addressed. E-mail: dstrout@alasu.edu.

10.1021/jp053490w CCC: $30.25

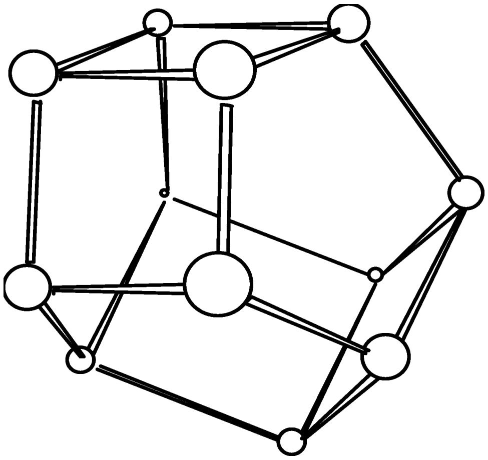

Figure 1. 0440 isomer of N_{12} (D_{2d} point group symmetry). The molecule has two pairs of edge-sharing four-membered rings.

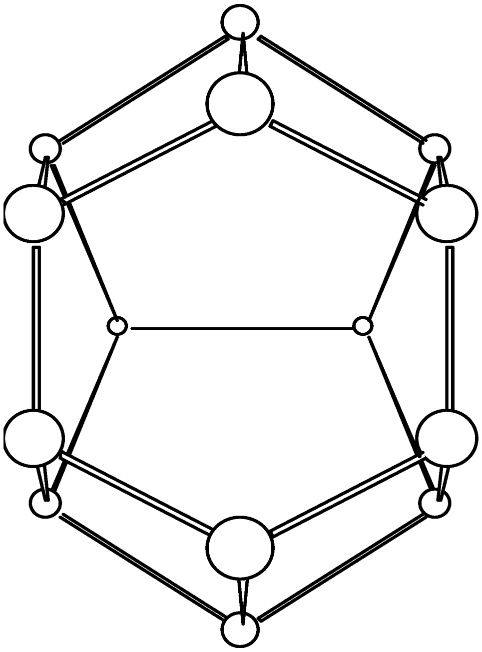

Figure 2. 0441 isomer of N_{14} (C_{2v} point group symmetry). The molecule has two pairs of edge-sharing four-membered rings.

(MP4(SDQ)). Each dissociation intermediate differs from its parent molecule only in the breaking of one bond. The intact molecules have a singlet ground state, and each of the dissociation intermediates has a triplet ground state. The basis set[26] is the correlation-consistent double-ζ set (cc-pVDZ) of Dunning. The Gaussian 03 quantum chemistry software package[27] is used for all calculations in this study.

Results and Discussion

Each of the nitrogen cages is subjected to oxygen insertion, using the minimum number of oxygens required to open all four-membered rings to pentagons and hexagons. The N_{12} 0440, N_{14} 0441, N_{14} 0522, and N_{16} 0604 cages become the insertion products $N_{12}O_2$, $N_{14}O_2$, $N_{14}O_3$, and $N_{16}O_4$, respectively. These oxygen insertion products are shown in Figures 5−8. Symmetry-independent bonds in each insertion product are labeled. For each insertion product, dissociation energies for each symmetry-independent bond are calculated using HF/cc-pVDZ and MP3/cc-pVDZ theories. Each dissociation intermediate has a triplet ground state with a large HOMO−LUMO gap, thereby implying a lack of low-lying excited states, which justifies the use of single-reference methods.

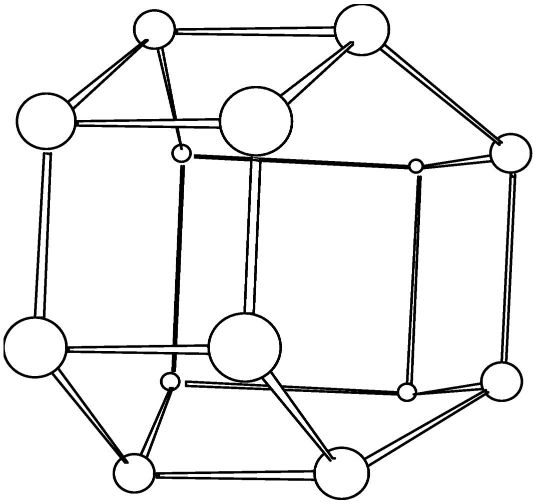

Figure 3. 0522 isomer of N_{14} (C_{2v} point group symmetry). The molecule has five four-membered rings as an edge-sharing pair and a band of three.

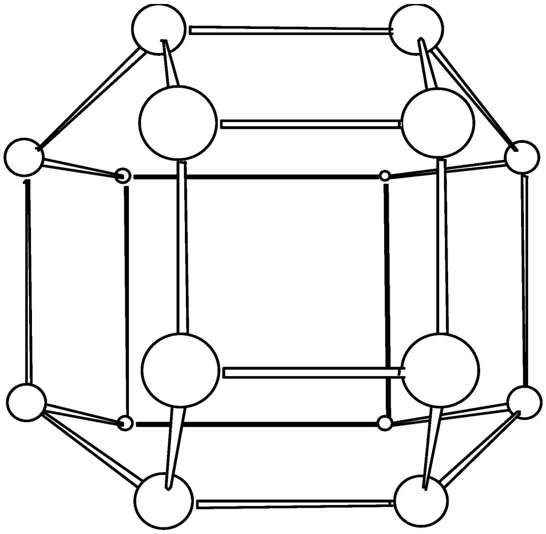

Figure 4. 0604 isomer of N_{16} (D_{2d} point group symmetry). The molecule has six four-membered rings as two bands of three.

The dissociation energies are tabulated for $N_{12}O_2$, $N_{14}O_2$, $N_{14}O_3$, and $N_{16}O_4$ in Tables 1−4, respectively. If, for each molecule, dissociation of the bond with the lowest dissociation energy is the first step in the decomposition in the molecule down to N_2 and O_2, then it is these "weakest link" energies that indicate the stability of the molecule. $N_{12}O_2$ has at least 30 kcal/mol resistance to dissociation in all of its bonds, according to MP4(SDQ) single-point calculations, irrespective of the choice of geometry. This molecule is likely a good candidate for HEDM. The $N_{12}O_2$ is a stable, high-energy molecule, but just what does "high energy" mean in quantitative terms? Table 5 shows the energy release properties of the oxygenated molecules in this study, and while none of them is as energetic as a pure nitrogen HEDM like N_{12}, the reductions in energy release are necessary tradeoffs for stability.

The oxygenated N_{14} molecules, $N_{14}O_2$ and $N_{14}O_3$, display an interesting contrast in terms of stability with respect to dissociation. On a "weakest link" basis, $N_{14}O_2$ is somewhat less stable than $N_{12}O_2$ (27.6 vs 36.4 kcal/mol resistance to dissociation at the MP3/cc-pVDZ level of theory). The comparable

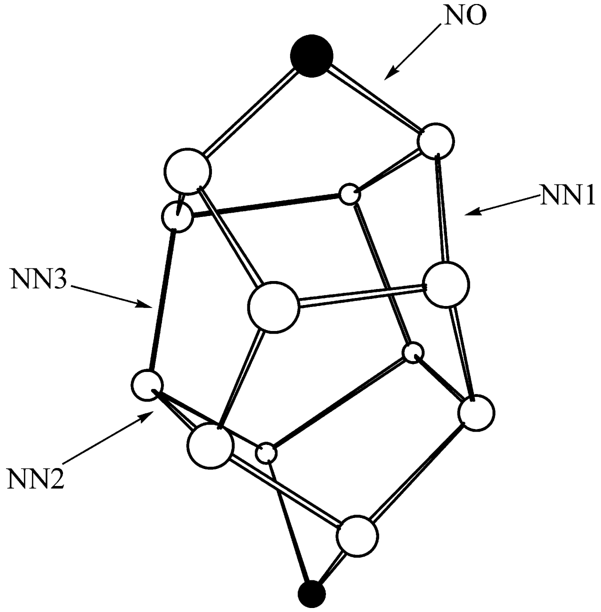

Figure 5. $N_{12}O_2$ molecule that results when N_{12} 0440 (Figure 1) has oxygen atoms inserted into bonds shared by four-membered rings. Symmetry-independent bonds in the molecule are labeled. The molecule has D_{2d} point group symmetry.

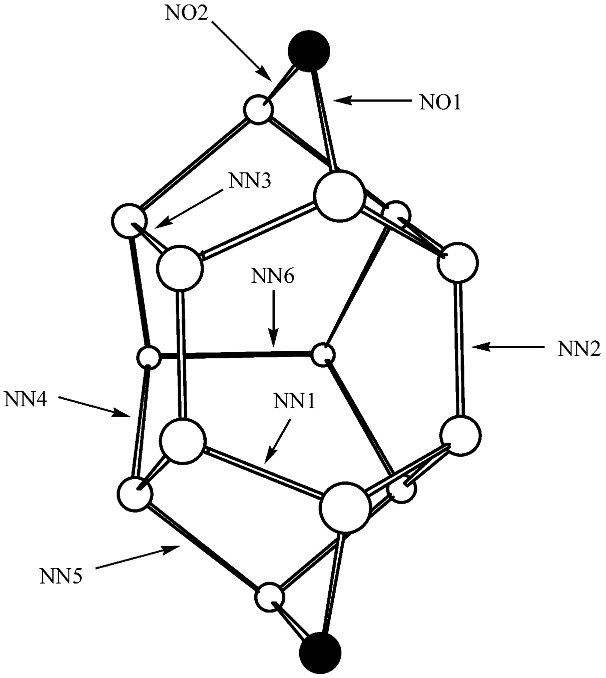

Figure 6. $N_{14}O_2$ molecule that results when N_{14} 0441 (Figure 2) has oxygen atoms inserted into bonds shared by four-membered rings. Symmetry-independent bonds in the molecule are labeled. The molecule has C_{2v} point group symmetry.

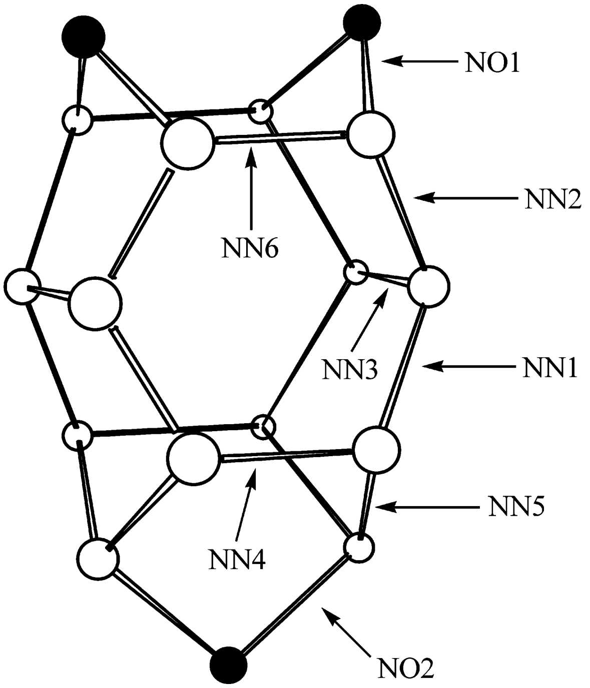

Figure 7. $N_{14}O_3$ molecule that results when N_{14} 0522 (Figure 3) has oxygen atoms inserted into bonds shared by four-membered rings. Symmetry-independent bonds in the molecule are labeled. The molecule has C_{2v} point group symmetry.

TABLE 1: Dissociation Energies[a] for $N_{12}O_2$ (bond labels from Figure 5) Calculated Using cc-pVDZ Basis Set

bond (Figure 5)	HF	MP3	MP4(SDQ)//HF	MP4(SDQ)//MP3
NO	+5.9	+36.4	+33.8	+33.3
NN1	+16.5	+47.6	+42.3	+44.9
NN2	+13.9	+46.6	+43.0	+45.3
NN3	+43.8	+70.6	+66.2	+67.5

[a] Energies are shown in kcal/mol.

TABLE 2: Dissociation Energies[a] for $N_{14}O_2$ (bond labels from Figure 6)

bond (Figure 6)	HF/cc-pVDZ	MP3/cc-pVDZ
NO1	+2.8	+33.6
NO2	−2.6	+31.4
NN1	−0.8	+27.6
NN2	+38.7	+63.4
NN3	+11.7	+42.5
NN4	+35.5	+61.6
NN5	+11.2	+40.3
NN6	+16.6	+47.7

[a] Energies are shown in kcal/mol.

TABLE 3: Dissociation Energies[a] for $N_{14}O_3$ (bond labels from Figure 7)

bond (Figure 7)	HF/cc-pVDZ	MP3/cc-pVDZ
NO1	−25.9	+10.2
NO2	+14.6	+45.3
NN1	+28.4	+52.0
NN2	+19.5	+47.3
NN3	+9.0	+43.2
NN4	+5.2	+30.3
NN5	+4.9	+35.8
NN6	−4.6	+23.3

[a] Energies are shown in kcal/mol.

stability between $N_{12}O_2$ and $N_{14}O_2$ is not surprising because of the structural similarities between the two molecules. However, the $N_{14}O_3$ is much less stable than either $N_{12}O_2$ or $N_{14}O_2$, because of the ease of dissociation of the NO1 bond (10.2 kcal/mol with MP3/cc-pVDZ). This NO1 bond is about 40 kcal/mol weaker than the NO2 bond, despite the fact that both are N−O single bonds. The difference between the NO1 and NO2 bonds of $N_{14}O_3$ is the proximity of another oxygen atom to an NO1 bond. Two electronegative oxygens in such close proximity (the 1 and 4 positions of a boat-conformed six-membered ring) may create a repulsion that is relieved by the breaking of an NO1 bond, hence the energetic favorability of the NO1-breaking process. Furthermore, the bond with the second-lowest dissociation energy is the NN6 bond, which is between the two mutually proximate oxygens. Breaking the NN6 bond is relatively favorable because it takes the proximate oxygens farther apart, which reduces the oxygen−oxygen repulsion.

TABLE 4: Dissociation Energies for $N_{16}O_4$ (bond labels from Figure 8)

bond (Figure 8)	HF/cc-pVDZ	MP3/cc-pVDZ
NO	−17.8	+18.1
NN1	−14.9	+15.8
NN2	+20.3	+43.6
NN3	+4.6	*a*
NN4	+25.2	+46.4

[a] Geometry optimization unsuccessful.

TABLE 5: Energy Release Properties of $N_{12}O_2$, $N_{14}O_2$, $N_{14}O_3$, and $N_{16}O_4$, with N_{12} Included for Comparison (energies calculated with MP3/cc-pVDZ)

molecule	reaction	kJ/mol	kJ/g
N_{12}[a]	$N_{12} \rightarrow 6N_2$	2209	13.1
$N_{12}O_2$	$N_{12}O_2 \rightarrow 6N_2 + O_2$	2135	10.7
$N_{14}O_2$	$N_{14}O_2 \rightarrow 7N_2 + O_2$	2604	11.4
$N_{14}O_3$	$N_{14}O_3 \rightarrow 7N_2 + (3/2)O_2$	2734	11.2
$N_{16}O_4$	$N_{16}O_4 \rightarrow 8N_2 + 2O_2$	3222	11.2

[a] The most stable N_{12} cage, designated as "2060" in ref 19.

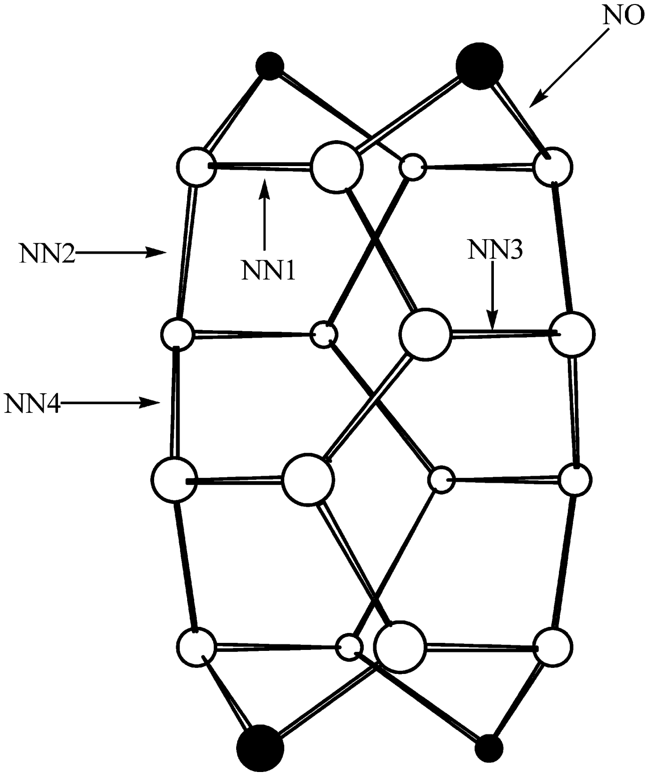

Figure 8. $N_{16}O_4$ molecule that results when N_{16} 0604 (Figure 4) has oxygen atoms inserted into bonds shared by four-membered rings. Symmetry-independent bonds in the molecule are labeled. The molecule has D_{2d} point group symmetry.

As a further demonstration of the effects of this oxygen−oxygen proximity, calculations have been performed on $N_{16}O_4$, shown in Figure 8. This molecule results from oxygenation of the four bonds of N_{16} (Figure 4) that are shared between four-membered rings. The bond-breaking energies in Table 4 show a low energy dissociation for both the NO bond and the nearby NN1 bond, 18.1 and 15.8 kcal/mol dissociation energy, respectively, at the MP3/cc-pVDZ level of theory. This molecule would most likely dissociate in the region near to the oxygens and not be a stable HEDM.

Conclusion

Cages of nitrogen that are otherwise unstable can be stabilized by oxygen insertion into N−N single bonds to relieve ring strain in some of the cage's polygons. However, only specific arrangements of inserted oxygen will be stabilizing. Oxygen atoms, with their polar bonds and high electronegativity, will likely repel one another if placed in close proximity within the cage structure. Proximity between oxygen atoms can lead to destabilization of the N−O bonds and the surrounding structure in the local area of the molecule. Therefore, although oxygen insertion is a viable means of stabilization of a nitrogen cage, the design of a practical HEDM requires that care be taken in the choice of arrangement of the inserted atoms. The $N_{12}O_2$ molecule has potential as a high-energy density material, as perhaps does the $N_{14}O_2$ molecule. The $N_{14}O_3$ and $N_{16}O_4$ molecules in this study have low-energy paths to dissociation and are not viable as HEDM.

Acknowledgment. The Alabama Supercomputer Authority is gratefully acknowledged for a grant of computer time on the SGI Altix in Huntsville, AL. This work was partially supported by the National Computational Science Alliance under Grant Nos. CHE030041 and CHE050022N and utilized the IBM p690 cluster in Champaign, IL. K.D.C. 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 5T34GM08167-20). D.L.S. is supported by MARC as a faculty research mentor. This work was also supported by the National Institutes of Health (NIH/NCMHD 1P20MD000547-01). The taxpayers of the state of Alabama in particular and the United States in general are gratefully acknowledged.

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