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Stabilization of an All-Nitrogen Molecule by Oxygen Insertion: Dissociation Pathways of N_8O_6

Douglas L. Strout*

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

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Nitrogen molecules N_x have been the subject of much recent research because of their potential as high energy density materials (HEDM). The reaction $N_x \rightarrow (x/2)\ N_2$ is exothermic by more than 50 kcal/mol per nitrogen atom. The difficulty in identifying practical nitrogen HEDM is that many small N_x molecules are not kinetically stable enough to serve as practical energy sources. Small three-coordinate N_x cages with all single bonds are especially unstable, due to the high angle strain and torsional strain of the molecules. However, the strain in these molecules can be relieved by the insertion of oxygen atoms into the N−N single bonds. For example, if an N_8 cube has oxygen inserted into all of its N−N bonds, a molecule of N_8O_{12} would result. The molecule would be much less strained than cubic N_8, but it may be possible to stabilize the N_8 cube with less than 12 oxygen atoms. In the present work, a molecule of N_8O_6 is examined by theoretical calculations to determine the energetics of its dissociation pathways. Calculations are performed with Hartree−Fock theory (HF) and Moller−Plesset perturbation theory (MP2 and MP4), and the basis sets are the correlation-consistent sets of Dunning. The stability of the N_8O_6 with respect to dissociation is discussed.

Introduction

Molecules consisting solely of nitrogen atoms have been studied extensively[1] as candidates for high energy density materials (HEDM). The dissociation of a molecule of N_x with all single bonds into molecules of N_2 would release more than 50 kcal/mol of energy per nitrogen atom.[2,3] The major problem in identifying nitrogen molecules to serve as practical HEDM is the issue of kinetic stability with respect to dissociation. Various linear and cyclic isomers of N_x have been shown by theoretical calculations[4−7] to dissociate too easily to be practical HEDM. Theoretical calculations on small, three-coordinate nitrogen cages[8−11] have predicted that tetrahedral N_4 may be metastable enough for an HEDM, but cubic N_8 dissociates with reaction barriers too low for an HEDM.

Significant advances have also taken place in the experimental synthesis of nitrogen molecules. The recent synthesis[12] 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[3] 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,[13] and a theoretical study[14] has suggested 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.

The greatest release of energy would come from an N_x molecule with all single bonds. However, most small nitrogen cages with all single bonds are kinetically unstable because of the angle strain and torsional strain in the bonds. It has been suggested[15] that insertion of oxygen atoms into the N−N single bonds would relieve the strain in the nitrogen cages. For example, oxygenation of the six bonds of an N_4 tetrahedron would result in a molecule of N_4O_6, and cubic N_8 would become N_8O_{12}. Such a nitrogen−oxygen molecule N_xO_y would still have all single bonds. Since there are no O−O bonds, the molecule would have $[(3x/2) - y]$ N−N bonds and $2y$ N−O bonds. The approximate energy release from such a molecule dissociating into N_2 and O_2 would be derived as follows (from bond energies[16] in kcal/mol):

$$N_xO_y\text{:}\ \ 59x + 37y \text{ kcal/mol bond energy}$$

$$(x/2)N_2 + (y/2)O_2\text{:}\ \ 113x + 60y \text{ kcal/mol bond energy}$$

$$\text{Energy release:}\ \ 54x + 23y \text{ kcal/mol}$$

On a per-atom basis, the nitrogen content of the molecule delivers over twice as much energy as the oxygen content (54 kcal/mol versus 23). Therefore, adding too many oxygen atoms will dilute the energy-producing power of the molecules. In designing molecules with optimal energy release properties, it is desirable to minimize the number of oxygen atoms, adding only that number required for stabilization of the molecule. In the current study, theoretical calculations are carried out on a cubic N_8 with only six of its twelve bonds oxygenated. Various dissociation pathways of the resulting N_8O_6 molecule are considered, and the energies of those pathways are calculated to determine how stable the N_8O_6 molecule is with respect to dissociation.

Computational Details

Geometry optimizations of N_8O_6 and its dissociation intermediates are carried out using Hartree−Fock theory (HF) and second-order perturbation theory[17] (MP2). Single energy points are carried out with fourth-order perturbation theory[17] (MP4(SDQ)). The calculations are performed with the double-ζ (CC-PVDZ) and augmented double-ζ (AUG-CC-PVDZ) basis sets[18]

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* E-mail: dstrout@asunet.alasu.edu.

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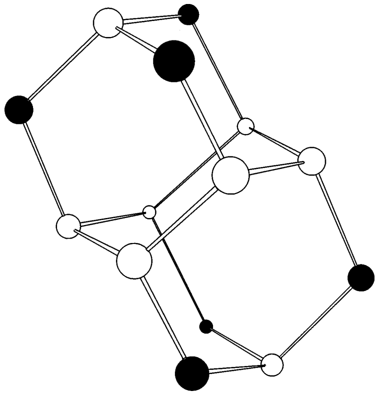

Figure 1. N_8O_6 cage molecule (D_{3d} symmetry, nitrogen atoms in white, oxygen atoms in black).

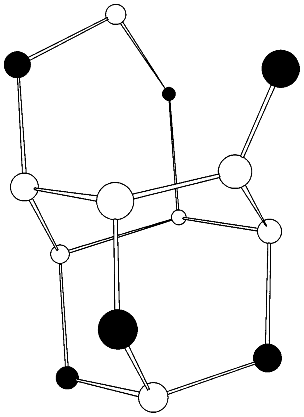

Figure 2. N_8O_6 intermediate with one "N−O-end" bond broken (C_s symmetry, nitrogen atoms in white, oxygen atoms in black).

of Dunning. Analytic frequencies for the N_8O_6 and its intermediates are calculated at the HF/CC-PVDZ level of theory. All calculations are carried out with the Gaussian 98 computational chemistry software package.[19]

Results and Discussion

The N_8O_6 molecule under consideration in this study is shown in Figure 1 and has a D_{3d} symmetry point group. This particular isomer is chosen because six-membered rings with a cyclohexane-like "chair" conformation have replaced all of the four-membered rings of the N_8 cube. The D_{3d} structure is confirmed as a minimum on the potential energy surface by HF/CC-PVDZ analytic frequencies. The molecule has three symmetry-independent bonds: an N−O bond to the N at the end of the molecule (designated "N−O-end"), an N−O bond to an N at the midsection of the molecule (designated "N−O-mid"), and an N−N bond around the midsection of the molecule (designated "N−N").

Breaking of an N−O-end bond results in the intermediate shown in Figure 2. This intermediate has C_s point group symmetry and a triplet ($^3A'$) electronic ground state. Breaking an N−O-mid bond results in the intermediate shown in Figure 3, which also has C_s symmetry and a triplet ($^3A'$) ground state. Breaking an N−N bond yields the intermediate shown in Figure 4, and that intermediate has C_2 point group symmetry and a triplet (^3B) ground state. Each of these bond-breaking intermediates is a confirmed minimum at the HF/CC-PVDZ level of theory.

The relative energies of the N_8O_6 cage molecule and these three bond-breaking intermediates are shown in Table 1. At every level of theory employed in this study, the intermediate with the N−O-end bond broken has the lowest energy of the three bond-breaking structures. In fact, the N−O-end bond-breaking process is slightly exothermic with Hartree−Fock theory. The MP2 energies of the intermediates are very much higher than the corresponding HF energies, with MP4 lowering the energies relative to the MP2 values. The MP4 bond-breaking energies are relatively insensitive to the choice of optimized geometry; the effect of choosing MP2 geometries versus HF geometries is only about 2 kcal/mol. The effect of the diffuse functions in the AUG-CC-PVDZ basis sets is to raise the relative energy of all the intermediates by 2−5 kcal/mol.

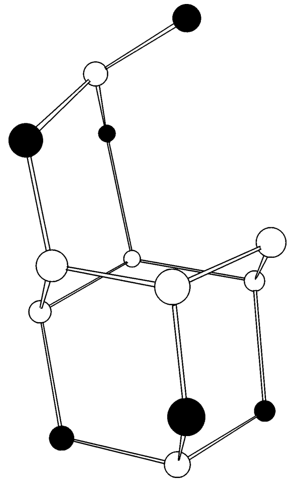

Figure 3. N_8O_6 intermediate with one "N−O-mid" bond broken (C_s symmetry, nitrogen atoms in white, oxygen atoms in black).

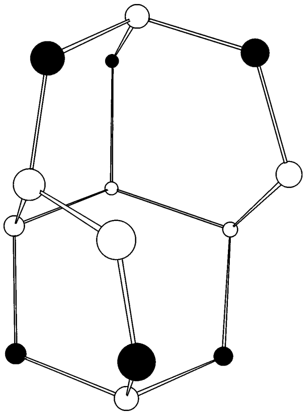

Figure 4. N_8O_6 intermediate with one "N−N" bond broken (C_2 symmetry, nitrogen atoms in white, oxygen atoms in black).

TABLE 1: Relative Energies of the N_8O_6 Molecule and Its One-Bond Dissociation Intermediates (energies in kcal/mol)

			bond breaking intermediates		
		cage	N−O-end	N−O-mid	N−N
HF	CC-PVDZ	0.0	−6.2	+12.1	+17.7
MP2	CC-PVDZ	0.0	+28.7	+39.3	+47.2
MP4//HF	CC-PVDZ	0.0	+18.7	+34.7	+37.4
MP4//MP2	CC-PVDZ	0.0	+20.8	+35.5	+39.4
HF	AUG-CC-PVDZ	0.0	−1.8	+15.2	+21.6
MP2	AUG-CC-PVDZ	0.0	+32.8	+43.8	+51.9
MP4//HF	AUG-CC-PVDZ	0.0	+21.4	+37.5	+41.2
MP4//MP2	AUG-CC-PVDZ	0.0	+24.2	+39.2	+43.4

Since the N−O-end intermediate is lowest in energy, it seems that the N−O-end bond is the most vulnerable to breaking. Breaking one of the N−O-end bonds is endothermic by less than 25 kcal/mol for all of the MP4 calculations in this study, which suggests that the N_8O_6 may dissociate too easily to be suitable as an HEDM. Is breaking of the N−O-end bond the

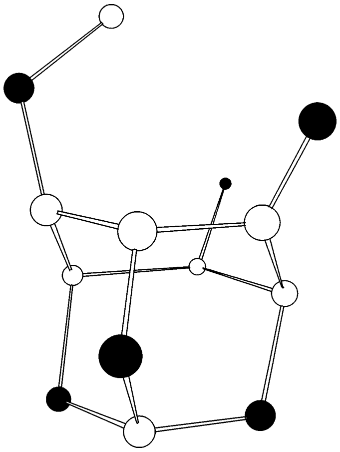

Figure 5. N_8O_6 intermediate with two "N−O-end" bonds broken (C_s symmetry, nitrogen atoms in white, oxygen atoms in black).

TABLE 2: Relative Energies of Minima along the Reaction Pathway for the N_8O_6 Molecule to Break Two N−O-end Bonds (energies in kcal/mol)

			no. of N−O-end bonds broken	
		cage	one bond	two bonds
HF	CC-PVDZ	0.0	−6.2	−23.4
MP2	CC-PVDZ	0.0	+28.7	+52.0
MP4//HF	CC-PVDZ	0.0	+18.7	+34.4
MP4//MP2	CC-PVDZ	0.0	+20.8	+37.9
HF	AUG-CC-PVDZ	0.0	−1.8	−14.9
MP2	AUG-CC-PVDZ	0.0	+32.8	+60.4
MP4//HF	AUG-CC-PVDZ	0.0	+21.4	+40.7
MP4//MP2	AUG-CC-PVDZ	0.0	+24.2	+44.8

first step in a facile dissociation mechanism for N_8O_6? If the N−O-end bond can be broken at a low energy, what would be a reasonable choice for the second reaction step in the breakdown of the N_8O_6? Since the N−O-end bond seems to be the most vulnerable to dissociation, an intermediate is considered with TWO bonds of this type broken. The structure of this two-bond-breaking intermediate is shown in Figure 5. This structure has C_s symmetry and a quintet ($^5A'$) electronic ground state. It has been confirmed as a minimum at the HF/CC-PVDZ level of theory. Using all of the methods applied to the one-bond-breaking intermediates, energies have been calculated for this intermediate with two N−O-end bonds broken.

The results for the two-bond-breaking intermediate are shown in Table 2. While the second N−O-end bond break is (like the first) exothermic with Hartree−Fock theory, higher levels of theory predict that the second bond break is (like the first) endothermic and leads to an even higher-energy intermediate. Therefore, N−O-end bond-breaking is a high-energy process, although two reaction steps are required to fully realize the endothermicity of that mechanism. Since the N−O-mid and N−N bond-breaking processes are endothermic in the first step by more than 30 kcal/mol, all three dissociation mechanisms pass through high-energy intermediates.

TABLE 3: HF/CC-PVDZ Energies (in hartrees) of Frontier Orbitals for N_8O_6 Cage and Dissociation Intermediates (orbitals of open-shell molecules are designated as α or β spin)

molecule	HOMOs	LUMOs
closed cage (Figure 1)	−0.46509	.19573
	−0.46509	.19573
	−0.51529	.21547
	−0.55522	.21547
	−0.55522	.22906
N−O-end intermediate (Figure 2)	−0.45487 (α)	.06687 (β)
	−0.46759 (β)	.09230 (β)
	−0.47149 (α)	.18045 (α)
	−0.48979 (β)	.18372 (β)
	−0.51687 (α)	.20906 (α)
N−O-mid intermediate (Figure 3)	−0.46062 (β)	.00106 (β)
	−0.46279 (α)	.07930 (β)
	−0.46633 (β)	.18239 (α)
	−0.47911 (α)	.18565 (β)
	−0.49523 (α)	.20111 (α)
N−N intermediate (Figure 4)	−0.43550 (α)	.05410 (β)
	−0.47860 (α)	.10179 (β)
	−0.47917 (β)	.18064 (α)
	−0.49004 (β)	.19331 (β)
	−0.49720 (α)	.20224 (α)
2-bond-breaking intermediate (Figure 5)	−0.45952 (α)	.04610 (β)
	−0.47031 (α)	.09401 (β)
	−0.47573 (β)	.10398 (β)
	−0.49350 (β)	.12465 (β)
	−0.51251 (α)	.19598 (α)

The likeliest explanation for the wide disagreement between HF and MP4 is the change of spin state between the N_8O_6 and the intermediates. Previous studies[5,6] of dissociation of N_x molecules have shown better agreement between HF and perturbation theory. However, those studies did not involve molecules in different spin states. Further, Tables 1 and 2 show that the largest disagreements between HF and MP4 occur for the two-bond-breaking intermediate with a quintet ground state. When computing energies relative to the closed-shell N_8O_6, the disagreement between HF and perturbation theory seems to roughly correlate to the number of unpaired electrons in the intermediates.

To assess the likelihood that these high-spin intermediates may have low-spin counterparts that are lower in energy, the HF/CC-PVDZ frontier orbital energies for the closed cage and each intermediate have been tabulated in Table 3. Relative to the closed cage, all of the intermediates show significant lowering of the energy for the lowest unoccupied molecular orbital (LUMO). However, all of the intermediates also have a low energy for the highest occupied molecular orbital (HOMO), and the HOMO−LUMO gaps for all of the intermediates are substantial (>0.4 hartrees). Therefore, these high-spin intermediates very likely represent the lowest-energy dissociation pathways for this isomer of N_8O_6.

Conclusion

An isomer of N_8O_6 formed by oxygenation of the N_8 cube has been shown to have significant resistance to dissociation for several dissociation mechanisms. Each dissociation pathway in this study passes through an intermediate with an energy at least 30 kcal/mol above the original N_8O_6 molecule. This N_8O_6 can release approximately 570 kcal/mol of energy[16] by dissociating into N_2 and O_2, and the molecule should be metastable enough to serve as a practical HEDM. Stabilization of the N_8 cube does not require oxygenation of all twelve bonds. The question remains open as to whether the cube can be stabilized by fewer than six oxygen atoms. Also, other N_x cages that are unstable should be examined as candidates for stabilization by oxygenation.

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