Beyond N$_8$O$_6$: Length Effects and End-Cap Effects on the Stability of a Hexagonal Nitrogen Tube

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A recent study suggested the possibility that a particular isomer of N$_8$O$_6$ is metastable enough to be a high-energy-density material (HEDM). Using that molecule as a starting point, other molecules are considered as HEDM candidates. The molecules in the current study are variations of N$_8$O$_6$, varied in two ways. First, length increases are considered, with the insertion of additional rings of nitrogen in a "tube" structure. Also, changes in the "end-cap" of N$_8$O$_6$ are considered, since the NO$_3$ "end-cap" is apparently the weakest site in the original N$_8$O$_6$ molecule. Stability with respect to bond breaking is determined by theoretical calculations of bond-breaking reactions. Hartree−Fock (HF) theory and perturbation theory (MP2 and MP4) are employed, along with the correlation-consistent basis sets of Dunning. Each molecule is examined to determine the lowest-energy pathway to dissociation. The major results are that a new end-cap can stabilize the molecule, but lengthening the "tube" structure actually weakens the molecule relative to N$_8$O$_6$.

Introduction

Nitrogen molecules N$_x$ and their cations and anions have attracted much attention for their potential as high-energy-density materials (HEDM), since the reaction N$_x$ → (x/2)N$_2$ is strongly exothermic, releasing over 50 kcal/mol per nitrogen atom. These molecules are being studied to determine their stability and factors that influence their stability. Numerous theoretical studies have characterized small nitrogen molecules as being too unstable to be practical energy sources. Cyclic and acyclic isomers with eight to twelve atoms have been studied[1−5] and shown to dissociate with low barriers, thereby demonstrating their instability. Cage isomers of N$_8$ and N$_{12}$ have also been shown[5−8] to have low-energy routes to dissociation.

Experimental progress in the observation and synthesis of nitrogen molecules has been encouraging. Whereas N$_2$ and the azide ion N$_3^-$ were once the only known all-nitrogen molecules, the N$_5^+$ cation has recently been produced[9] in the laboratory. That result prompted a theoretical study[10] of N$_8$ molecules resulting from the addition of the N$_5^+$ and the azide ion. The N$_8$ addition products were shown to dissociate with sufficiently low barriers that they are unlikely to be stable HEDM. The N$_5^-$ anion has also been produced[11,12] in the laboratory, and a recent theoretical study[13] has suggested that an N$_5^+$/N$_5^-$ ion pair may be a useful form of N$_{10}$.

One of the factors tending to destabilize small N$_x$ cage molecules is the angular strain in the three- and four-membered rings in the cage network. It has been suggested[14] 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[15,16] of oxygenation of the N$_8$ cubic molecule indicate that there exists an N$_8$O$_6$ which may be stable enough to be a useful HEDM, but several isomers of N$_8$O$_4$ 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.

Can the previous N$_8$O$_6$ molecule be used for a model for even larger HEDM candidates with an even larger concentration of nitrogen (and therefore greater per-atom energy delivery)? The N$_8$O$_6$ molecule from the previous study can be viewed as a ring of six nitrogens with an NO$_3$ end-cap on both ends. Inserting another ring of six nitrogens would yield a molecule of N$_{14}$O$_6$, and further insertions of nitrogen rings would lead to progressively longer tube-shaped nitrogen molecules. The stability of such molecules will be determined by theoretical calculations. Also, since the weakest bond of the previously studied N$_8$O$_6$ is an N−O bond in the end-cap, an alternative end-cap is considered in which a carbon atom is substituted for the nitrogen on the end of the molecule. The stability of the molecules with this alternate end-cap is compared to the original N$_8$O$_6$.

Computational Details

Geometries are optimized with Hartree−Fock (HF) and second-order Moller−Plesset perturbation theory[17] (MP2). Single-point energies are calculated with fourth-order Moller−Plesset perturbation theory[17] (MP4). Intact molecules are optimized in their singlet ground states, and each dissociation intermediate is optimized in the triplet state, which is the ground state. The basis sets are the correlation-consistent polarized double-ζ (CC−PVDZ) of Dunning[18] and the augmented double-ζ set (AUG−CC−PVDZ). Calculations are carried out using the Gaussian 98 and Gaussian 03 quantum chemistry software packages.[19,20]
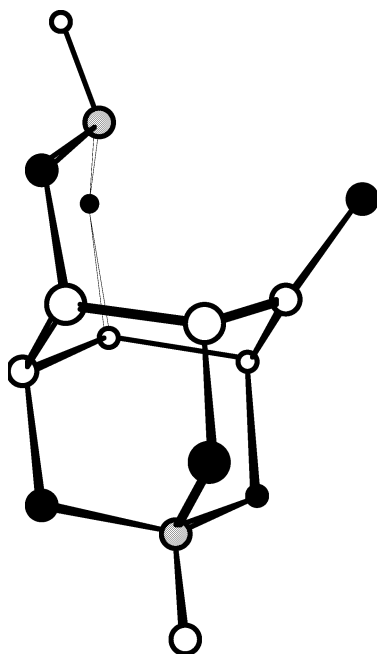
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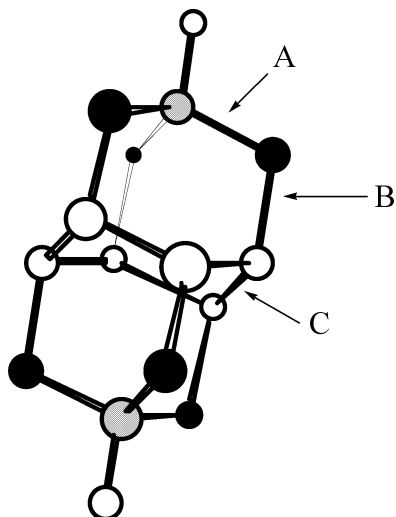
Figure 1. $N_6O_6C_2H_2$ molecule (D_{3d} symmetry point group). Symmetry-independent bonds are labeled as (A) C—O bond, (B) N—O bond, and (C) N—N bond. These alphabetic labels are used in Table 1. (Nitrogen atoms are shown in white, oxygen black, carbon gray, and a white hydrogen atom appears at both ends of the molecule.)
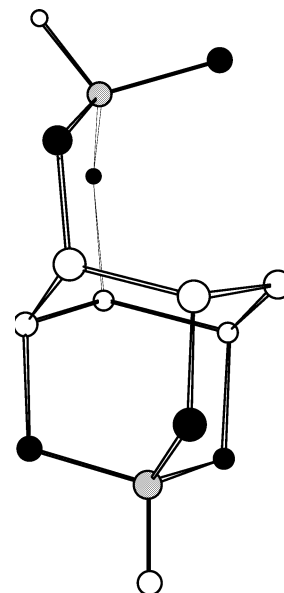

Figure 3. $N_6O_6C_2H_2$ dissociation intermediate with an N—O bond broken. (Nitrogen atoms are shown in white, oxygen black, carbon gray, and a white hydrogen atom appears at both ends of the molecule.)

Figure 2. $N_6O_6C_2H_2$ dissociation intermediate with a C—O bond broken. (Nitrogen atoms are shown in white, oxygen black, carbon gray, and a white hydrogen atom appears at both ends of the molecule.)

Figure 4. $N_6O_6C_2H_2$ dissociation intermediate with an N—N bond broken. (Nitrogen atoms are shown in white, oxygen black, carbon gray, and a white hydrogen atom appears at both ends of the molecule.)
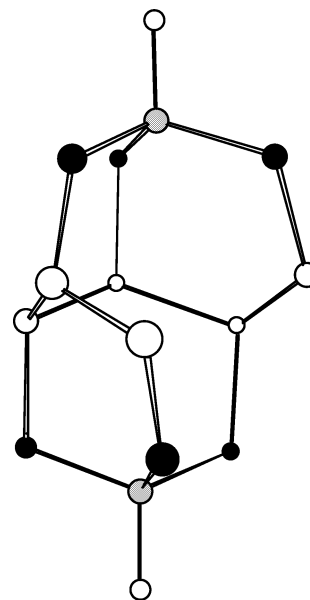
Results and Discussion

Effects of a Carbon End-Cap. Figure 1 shows a molecule with a carbon atom at either end bonded to three oxygens, with a ring of six nitrogens in the middle. This is the variation of N_8O_6 with carbon end-caps (a hydrogen atom has been added to each end to provide the fourth bond to carbon). The molecule has the formula $N_6O_6C_2H_2$ and belongs to the D_{3d} symmetry point group. The molecule has three symmetry-independent bonds between heavy atoms: the C—O bond, the N—O bond, and the N—N bond. Bond-breaking intermediates for the three symmetry-independent bonds are depicted in Figures 2, 3, and 4, respectively.

Dissociation energies for all three bonds are shown in Table 1. As with the N_8O_6 molecule, the HF dissociation energies are low relative to MP2 and MP4. This contrast between HF and

TABLE 1: Bond-Breaking Energies of $N_6O_6C_2H_2$ (energies in kcal/mol)[a]

method	basis set	C—O bond (A)	N—O bond (B)	N—N bond (C)
HF	CC—PVDZ	+46.3	+27.6	+11.2
MP2	CC—PVDZ	+72.6	+72.8	+43.1
MP4//HF	CC—PVDZ	+66.0	+60.0	+32.5
MP4//MP2	CC—PVDZ	+67.1	+60.9	+34.6
HF	AUG—CC—PVDZ	+49.0	+29.6	+14.7
MP2	AUG—CC—PVDZ	+74.8	+76.0	+47.3
MP4//HF	AUG—CC—PVDZ	+67.5	+62.1	+35.7
MP4//MP2	AUG—CC—PVDZ	+68.9	+63.1	+38.0

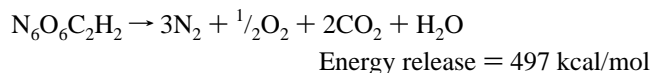[a] Alphabetic bond labels refer to Figure 1.

MP2 and MP4 is most likely due to the change of spin state between the intact molecule and the dissociation intermediates, and the effect has been documented in the N_8O_6 study.[15] As in the N_8O_6 study, all of the dissociation intermediates have large
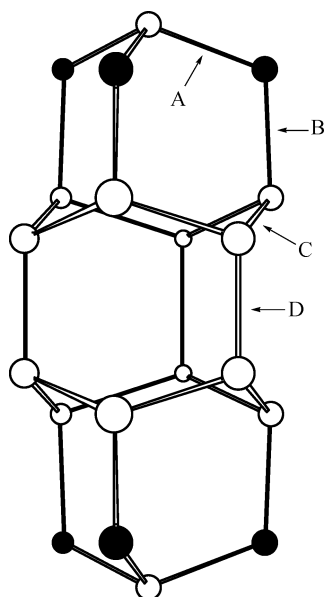
Figure 5. N$_{14}$O$_6$ molecule (D_{3h} symmetry point group). Symmetry-independent bonds are labeled as (A) N−O bond on end-cap, (B) N−O bond on the side of the molecule, (C) N−N bond within a ring of nitrogen, and (D) N−N bond between two rings of nitrogen. (Nitrogen atoms are shown in white, and oxygen atoms are shown in black.)

Figure 6. N$_{12}$O$_6$C$_2$H$_2$ molecule (D_{3h} symmetry point group). Symmetry-independent bonds are labeled as (A) C−O bond on end-cap, (B) N−O bond on the side of the molecule, (C) N−N bond within a ring of nitrogen, and (D) N−N bond between two rings of nitrogen. (Nitrogen atoms are shown in white, oxygen black, carbon gray, and a white hydrogen atom appears at both ends of the molecule.)

HOMO−LUMO gaps, which suggests that the single-reference approach used in this study should be reasonably accurate. By contrast with N$_8$O$_6$, none of the bond breaks in N$_6$C$_2$O$_6$H$_2$ are predicted by HF to be exothermic. All bond breaks are endothermic with HF theory, and MP2 and MP4 give endothermicities that are even greater. MP2 energies are much greater than HF energies, with a moderate lowering of the energies by MP4 relative to MP2. The diffuse functions in the AUG−CC−PVDZ basis set have the effect of raising the dissociation energies by a few kcal/mol across the board. Most importantly, at the MP4 level of theory, all dissociations are endothermic by more than 30 kcal/mol, indicating that the N$_6$O$_6$C$_2$H$_2$ may be a viable high-energy-density material (HEDM). Replacing the relatively weak N−O end-cap bonds of N$_8$O$_6$ with C−O bonds has strengthened the molecule overall. The lowest energy dissociation for N$_6$O$_6$C$_2$H$_2$ is endothermic by 35−40 kcal/mol (compared to 20−25 kcal/mol for N$_8$O$_6$ (ref 15)), which indicates more resistance to dissociation than the corresponding N$_8$O$_6$.

What is the effect of the carbon end-cap on the energy delivery of the molecule as it decomposes? Bond energy comparison[21] of the two reactions indicates the following:

$$N_8O_6 \rightarrow 4N_2 + 3O_2 \quad \text{Energy release} = 577 \text{ kcal/mol}$$

$$N_6O_6C_2H_2 \rightarrow 3N_2 + {}^1/_2O_2 + 2CO_2 + H_2O$$
$$\text{Energy release} = 497 \text{ kcal/mol}$$

Replacing the nitrogen end-cap with a carbon end-cap results in approximately a 15% loss of energy release per molecule, but the enhanced stability of the molecule is still advantageous to a high-energy-density material (HEDM).

Length Effects: Insertion of the Second Nitrogen Ring. For either N$_8$O$_6$ or N$_6$O$_6$C$_2$H$_2$, an end-cap may be removed, a second ring of six nitrogens added, and the end-cap reattached. The resulting molecules would have the formulas N$_{14}$O$_6$ and N$_{12}$O$_6$C$_2$H$_2$, respectively, and a correspondingly higher concentration of nitrogen atoms than their respective predecessors. These two molecules are pictured in Figures 5 and 6. Both N$_{14}$O$_6$
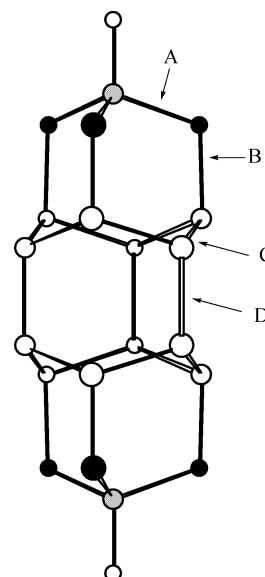
TABLE 2: Bond-Breaking Energies for N$_{14}$O$_6$ and N$_{12}$O$_6$C$_2$H$_2$ (energies in kcal/mol)[a]

		N$_{14}$O$_6$	N$_{12}$O$_6$C$_2$H$_2$
HF/CC−PVDZ	N−O (C−O) end-cap (A)	−12.6	+40.8
	N−O alongside (B)	+10.4	+26.2
	N−N within ring (C)	+2.9	−1.0
	N−N ring−ring (D)	+46.5	+47.6
MP2/CC−PVDZ	N−O (C−O) end-cap (A)	+25.6	+69.6
	N−O alongside (B)	+32.7	+70.0
	N−N within ring (C)	+32.6	+29.8
	N−N ring−ring (D)	+78.2	+81.5

[a] Alphabetic bond labels refer to Figure 5 for N$_{14}$O$_6$ and Figure 6 for N$_{12}$O$_6$C$_2$H$_2$.

and N$_{12}$O$_6$C$_2$H$_2$ belong to the D_{3h} point group and have four symmetry-independent bonds, namely an N−O (or C−O) end-cap bond, and N−O bond along the side of the molecule, an N−N bond within a ring of nitrogen and an N−N bond between the two rings of nitrogen.

Bond-breaking energies are shown in Table 2. Both molecules show weakening of the structure (lowering of the bond dissociation energies), relative to their one-ring counterparts. N$_{14}$O$_6$ shows the weakest bond to be in the end-cap, as it is with N$_8$O$_6$, but at the MP2/CC−PVDZ level of theory, N$_{14}$O$_6$ dissociates with an energy of 26 kcal/mol as opposed to 29 kcal/mol at the corresponding level of theory for N$_8$O$_6$. The effect is even more pronounced for N$_{12}$O$_6$C$_2$H$_2$, which dissociates a bond within the nitrogen ring at an energy of 30 kcal/mol versus 43 kcal/mol for a similar bond in the smaller N$_6$O$_6$C$_2$H$_2$. Considering that MP4 energy points would likely lower all of the bond dissociation energies for both N$_{14}$O$_6$ and N$_{12}$O$_6$C$_2$H$_2$, it is likely that both molecules dissociate too easily to hold promise as HEDM.

Third Ring of Nitrogen. The structural weakening calculated with the second ring of nitrogen is even more pronounced for the third ring. Bond dissociation energies for a molecule (molecular formula N$_{18}$O$_6$C$_2$H$_2$, shown in Figure 7) with three rings of nitrogen and carbon end-caps are shown in Table 3. The weakest bond in this molecule is the N−N bond in the center ring of the molecule. This bond dissociates with energy
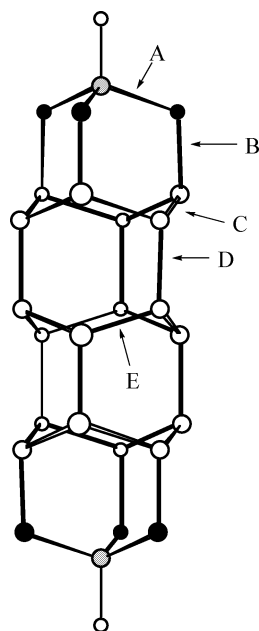
Figure 7. $N_{18}O_6C_2H_2$ molecule (D_{3h} symmetry point group). Symmetry-independent bonds are labeled as (A) C—O bond on end-cap, (B) N—O bond on the side of the molecule, (C) N—N bond within the end-most ring of nitrogen, (D) N—N bond between two rings of nitrogen, and (E) N—N bond within the central ring of nitrogen. (Nitrogen atoms are shown in white, oxygen black, carbon gray, and a white hydrogen atom appears at both ends of the molecule.)

TABLE 3: Bond-Breaking Energies for $N_{18}O_6C_2H_2$ (energies in kcal/mol)

		$N_{18}O_6C_2H_2$
HF/CC—PVDZ	C—O bond (A)	+40.6
	N—O bond (B)	+19.4
	N—N bond within end ring (C)	−1.5
	N—N bond between rings (D)	+42.6
	N—N within center ring (E)	−12.6
MP2/CC—PVDZ	C—O bond (A)	+69.7
	N—O bond (B)	+57.7
	N—N bond within end ring (C)	*b*
	N—N bond between rings (D)	+66.2
	N—N within center ring (E)	+16.5

a Alphabetic bond labels refer to Figure 7. *b* Geometry optimization was unsuccessful.

of only 16.5 kcal/mol at the MP2 level of theory, with further lowering expected if the MP4 energy were calculated. As the length of the tube-shaped nitrogen structure increases, the strength of the structure with respect to dissociation decreases, which would indicate that long tubes of hexagonal nitrogen are likely not to be promising high-energy-density materials.

The molecules in this study show another trend in terms of the exact position of the weakest bond. Using the series of carbon-capped molecules to illustrate, in $N_6O_6C_2H_2$, the weakest bond is in the N—N ring. In the $N_{12}O_6C_2H_2$, the weakest bond is in an N—N ring that is adjacent to another N—N ring. Finally, in the large $N_{18}O_6C_2H_2$ molecule, the weakest bond is an N—N bond in a ring between two other nitrogen rings. Is there a structural cause for this bond weakening? Table 4 shows the values for symmetry-independent angles in the $N_{18}C_2O_6H_2$, and the angles around the center ring of nitrogen are not especially remarkable. There are no strong deviations from tetrahedral angles, so angle strain is not a likely contributor to the weakness of the central bonds. The trend indicates that the N—N bond is weakened by the proximity of other rings of nitrogen. In other words, the N—N bonds in the rings are strengthened in the presence of the electronegative oxygen atoms.

TABLE 4: Symmetry-Independent Angles for $N_{18}C_2O_6H_2$ Molecule (angles in degrees)^a

angle	HF/CC—PVDZ	MP2/CC—PVDZ
O—C—O	110.0	111.5
C—O—N1	110.8	110.1
O—N1—N1	106.6	104.7
N1—N1—N1^b	111.0/111.8	112.1/113.1
N1—N1—N2	107.3	105.8
N1—N2—N2	107.8	106.2
N2—N2—N2	111.3	112.8

a N1 denotes a nitrogen atom in an outer ring, and N2 denotes a nitrogen atom in the center ring. *b* Two symmetry-independent N1—N1—N1 angles exist.

Conclusion

The weakness of N_8O_6 with respect to dissociation in its NO_3 end-cap can be remedied by substitution of an analogous carbon-based end-cap. The insertion of the second ring of nitrogen had a substantial weakening effect on the N—N bonds composing each nitrogen ring. Insertion of a third ring weakened the structure even further, such that bonds at the midsection of the $N_{18}O_6C_2H_2$ are susceptible to dissociation at low energy. It seems that the N—N bond is strengthened by the polar environment near the oxygens in the end-cap, and the more an N—N bond is surrounded by a nonpolar all-nitrogen environment, the weaker the N—N bond will become. This would suggest that the best candidates for nitrogen cage HEDM are smaller molecules that also contain highly electronegative atoms, such as the oxygens in the stable $N_6O_6C_2H_2$ molecule.

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