

Are Four Oxygens Enough to Stabilize the N₈ Cube? Dissociation Pathways of Cage Isomers of N₈O₄

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Various all-nitrogen molecules have been examined as candidates for high energy density materials (HEDM), because of the energy release that would accompany the dissociation of such a molecule down to N₂ molecules. Numerous molecules N_x have been shown to dissociate too easily to be a viable HEDM, including small N_x all-nitrogen cages. One possible solution to the instability of small N_x cages is oxygen insertion into the N–N bonds. Conversion of N–N bonds into N–O–N bonding groups would relieve much of the ring strain in small N_x cages, thereby stabilizing the molecule and possibly making the N_xO_y molecule a good HEDM. Several cage isomers of N₈O₄ are examined by theoretical calculations to evaluate their suitability as potential HEDM. Calculations are carried out with Hartree–Fock theory and Møller–Plesset perturbation theory (MP3 and MP4), using the CC-PVDZ basis set of Dunning. The relative thermodynamic stability of the isomers is discussed, along with dissociation energies for the various N₈O₄ cages.

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 → (x/2)N₂, 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 suggested¹ 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 8–12 nitrogen atoms. Cage isomers of N₈ and N₁₂ 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 synthesis⁹ of the N₅⁺ cation has opened new possibilities for production of all-nitrogen molecules. The production of N₅⁺ also led to a theoretical study¹⁰ of N₈ molecules that could be produced by an addition reaction between the N₅⁺ ion and the N₃[–] azide ion. None of the N₈ products was judged to be stable enough to be a practical HEDM. Also, the N₅[–] anion has been experimentally synthesized,¹¹ and a theoretical study has suggested¹² that an N₅⁺/N₅[–] 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.

It has been suggested¹³ that nitrogen cages could be stabilized by insertion of oxygen atoms into the N–N bonds. The molecule would still have all single bonds, N–N and N–O bonds. The resulting N_xO_y molecules would have less ring strain than their N_x counterparts, with the N_xO_y molecule possibly being a suitable candidate for HEDM. Dissociation pathways for a cage isomer of N₈O₆ have been examined,¹⁴ and the dissociation energies of that molecule were found to be high enough for an

HEDM. Although the oxygen atoms can stabilize the nitrogen cage, the oxygen atoms also dilute the energy release properties of the molecules. For a nitrogen–oxygen molecule N_xO_y that undergoes the reaction N_xO_y → (x/2)N₂ + (y/2)O₂, bond strength analysis¹⁵ indicates that the per-atom energy release is more than twice as great for nitrogen atoms as for oxygen atoms. Optimal design of a nitrogen–oxygen HEDM would therefore favor a molecule with the highest possible nitrogen content, containing only enough oxygen atoms to ensure stability.

In the current study, the ability of oxygen atoms to stabilize the N₈ cube is tested by theoretical calculations on dissociation pathways of N₈O₄ cages. Various cage isomers are generated by the oxygenation of four N–N single bonds of the N₈ cubic structure. Since the six oxygen atoms of the previously studied N₈O₆ are apparently sufficient¹⁴ to stabilize the structure, the remaining open question is whether stable structures exist with fewer than six oxygens.

Computational Details

Geometry optimizations of the various isomers of N₈O₆ and their dissociation intermediates are carried out using the Hartree–Fock (HF) method and third-order Møller–Plesset perturbation theory¹⁶ (MP3). (Second-order MP2 optimizations failed for several of the molecules in this study, mainly because MP2 tends to lengthen bonds relative to HF theory. This bond lengthening can lead to dissociative geometry optimizations.) The HF and MP3 geometries are used for single energy calculations with fourth-order perturbation theory (MP4(SDQ)). All calculations in this study are carried out with the CC-PVDZ basis set of Dunning.¹⁷ Previous studies^{6,7,14} have shown that the basis set effects from using larger basis sets are relatively small. All structures in this study are the result of optimization to local minima. The Gaussian 98 quantum chemistry software¹⁸ is used for all calculations in this study.

Results and Discussion

N₈O₄ Cage Isomers. The seven cage isomers under consideration in this study are labeled A through G and are shown in

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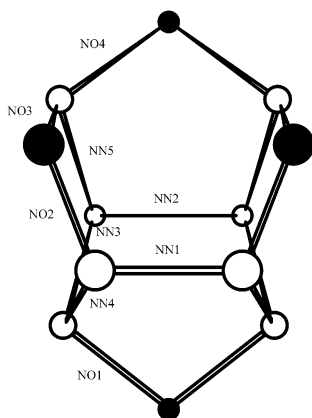


Figure 1. N_8O_4 isomer A. The molecule has C_s point group symmetry, and symmetry-independent bonds are labeled (nitrogen atoms in white, oxygen atoms in black).

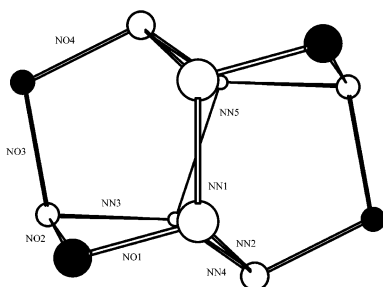


Figure 2. N_8O_4 isomer B. The molecule has C_2 point group symmetry, and symmetry-independent bonds are labeled (nitrogen atoms in white, oxygen atoms in black).

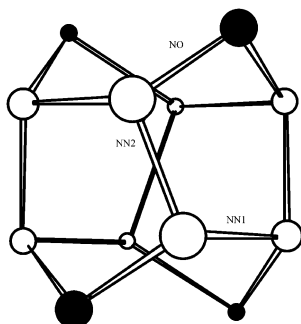


Figure 3. N_8O_4 isomer C. The molecule has D_{2d} point group symmetry, and symmetry-independent bonds are labeled (nitrogen atoms in white, oxygen atoms in black).

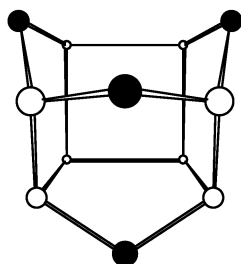


Figure 4. N_8O_4 isomer D. The molecule has C_s point group symmetry (nitrogen atoms in white, oxygen atoms in black).

Figures 1–7, respectively. All seven isomers are generated by the oxygenation of four N–N bonds on the N_8 cube. Isomer A has C_s point group symmetry, isomer B has C_2 symmetry, and isomer C has D_{2d} symmetry. Isomers A, B, and C also have no intact four-membered nitrogen rings; in each isomer, all six four-membered rings of the N_8 cube have been opened by oxygenation. Isomer D has C_s symmetry and one intact four-membered

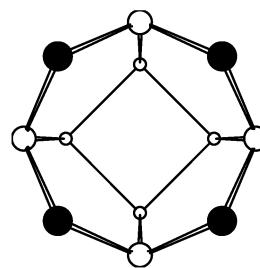


Figure 5. N_8O_4 isomer E. The molecule has C_{4v} point group symmetry (nitrogen atoms in white, oxygen atoms in black).

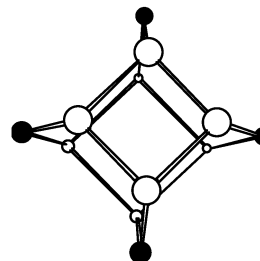


Figure 6. N_8O_4 isomer F. The molecule has D_{4h} point group symmetry (nitrogen atoms in white, oxygen atoms in black).

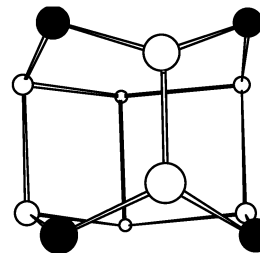


Figure 7. N_8O_4 isomer G. The molecule has C_{2v} point group symmetry (nitrogen atoms in white, oxygen atoms in black).

TABLE 1: Relative Energies (kcal/mol) of N_8O_4 Isomers (Calculations with CC-PVDZ Basis Set)

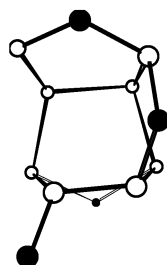
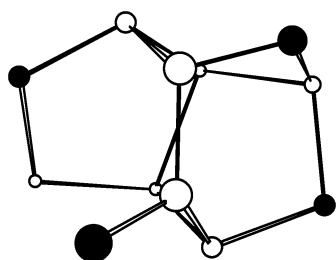
isomer	symmetry	no. of squares	HF	MP3	MP4//MP3
A	C_s	0	0.0	0.0	0.0
B	C_2	0	+7.9	+9.1	+10.6
C	D_{2d}	0	+8.9	+7.8	+7.6
D	C_s	1	+23.2	+24.6	+24.7
E	C_{4v}	1	+26.4	+28.5	+29.0
F	D_{4h}	2	+59.6	+63.2	+64.7
G	C_{2v}	2	+66.8	+68.8	+70.6

ring. Isomer E also has a four-membered ring and has C_{4v} symmetry. Isomers F and G have two four-membered rings each; isomer F has D_{4h} symmetry, and isomer G has C_{2v} symmetry. The geometries of all seven isomers were optimized at the HF/CC-PVDZ and MP3/CC-PVDZ levels of theory, and MP4-(SDQ)/CC-PVDZ single energies were calculated with the MP3/CC-PVDZ geometries. The relative energies of the seven molecules are tabulated in Table 1. The relative energies correlate to the number of four-membered nitrogen rings in each molecule. Isomers A, B, and C are lowest in energy and roughly isoenergetic. Isomers F and G are very much higher in energy than A, B, or C, with isomers D and E energetically in the middle, relative to the other five molecules. (Confirmation of the relative energies by coupled-cluster theory would be useful, but such calculations are beyond available computational resources.)

Bond-Breaking Studies. Only isomers A, B, and C are chosen for detailed bond-breaking studies, since they are the lowest in energy and therefore the likeliest candidates for a stable

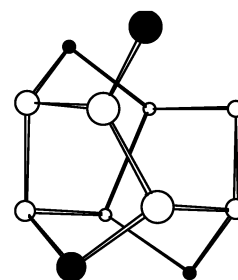
TABLE 2: HF/CC-PVDZ Dissociation Energies for N₈O₄ Isomers A, B, and C

isomer	broken bond	energy, kcal/mol	isomer	broken bond	energy, kcal/mol	
A	NN1	+4.7	B	NN3	+19.8	
	NN2	+11.6		NN4	+18.0	
	NN3	+13.1		NN5	+4.8	
	NN4	+14.3		NO1	+3.7	
	NN5	+34.1		NO2	-17.5	
	NO1	+10.1		NO3	-2.7	
	NO2	+3.5		NO4	+4.5	
	NO3	-16.4		C	NN1	+4.5
	NO4	+1.4			NN2	+27.1
B	NN1	-6.2	NO		-2.4	
	NN2	+5.2				

**Figure 8.** Isomer A with an NO3 bond broken. The NO3 break is the first step in the dissociation of isomer A (nitrogen atoms in white, oxygen atoms in black).**Figure 9.** Isomer B with an NO2 bond broken. The NO2 break is the first step in the dissociation of isomer B (nitrogen atoms in white, oxygen atoms in black).

HEDM. Isomer A and isomer B each have nine symmetry-independent bonds, and isomer C has three. The symmetry-independent bonds have been labeled in Figures 1–3. For each bond, dissociation energies have been calculated at the HF/CC-PVDZ level of theory. Following the labels shown in Figures 1–3, the dissociation energies are shown in Table 2. Each of the bond breaks tabulated in Table 2 leads to an intermediate with a triplet ground state. Each N₈O₄ isomer has at least one bond break that is exothermic with HF/CC-PVDZ, just as the previously studied N₈O₆ isomer did. The N₈O₆ study¹⁴ indicated that the bond break that was exothermic at the HF level of theory was also the lowest energy bond break when calculated at higher levels of theory. For each N₈O₄ isomer, the lowest energy bond break is that of a nitrogen–oxygen bond, another feature in common between N₈O₄ and N₈O₆.

For isomers A, B, and C, the bond break that is most exothermic at the HF/CC-PVDZ level of theory has been subjected to calculations at higher levels of theory. The bond-breaking intermediates for isomer A, B, and C are shown in Figures 8–10, respectively. The geometries of the cage molecules and their bond-breaking intermediates have been optimized at the MP3/CC-PVDZ level of theory, and single energies have been calculated with MP4/CC-PVDZ at both the HF and MP3 geometries. The results have been tabulated in Table 3. In each case, the MP4 bond-breaking energies are below the 30 kcal/mol threshold that has been suggested as a criterion for a metastable HEDM. Therefore, each isomer has one bond break

**Figure 10.** Isomer C with an NO bond broken. The NO break is the first step in the dissociation of isomer C (nitrogen atoms in white, oxygen atoms in black).**TABLE 3: Bond-Breaking Energies for N₈O₄ Cage Isomers^a**

isomer	bond	HF	MP3	MP4/HF	MP4/MP3
A	NO3	-16.4	+19.8	+15.7	+18.4
B	NO2	-17.5	+16.1	+11.2	+13.8
C	NO	-2.4	+28.9	+24.8	+26.9

^a Energies in kcal/mol, all calculations carried out with CC–PVDZ basis set.

TABLE 4: Energies of Two Bond Breaking Intermediates of the N₈O₄ Cages^a

isomer	1st break	2nd break	HF	MP3	MP4/HF	MP4/MP3
A	NO3	NN3	-34.7	+0.6	-5.5	-4.5
B	NO2	NN5	-21.1	+14.3	+5.9	+8.5
C	NO	NO	-20.1	+6.5	+1.2	+1.2

^a Energies in kcal/mol relative to original cage, all calculations carried out with CC-PVDZ basis set.

that may be the first step in the facile dissociation of the molecule into the final products N₂ and O₂.

The previously studied N₈O₆ was also shown to have a bond dissociation with less than a 30 kcal/mol dissociation energy, but the second step in the dissociation was also shown to be endothermic, so that all dissociation paths for N₈O₆ were shown to involve at least one high-energy intermediate. Is the same true for these N₈O₄ isomers? For each of the dissociation intermediates for isomers A, B, and C, an intermediate with a second bond broken is optimized with the HF/CC-PVDZ and MP3/CC-PVDZ methods. In each case, the second bond to be broken is chosen such that an N₂ edge is exposed, with an N=N double bond. Such an intermediate, which could lead to the breakout of an N₂ molecule, should be low in energy and provide the most stringent test for the stability of the N₈O₄ molecules. The energies of the two-bond-breaking intermediates are shown in Table 4. Each isomer (A, B, and C) has an intermediate with two broken bonds such that the second bond-breaking step is exothermic. The intermediates all have triplet ground states and are low in energy relative to the corresponding original cage isomers. Therefore, none of the N₈O₄ isomers in this study are stable enough to be a viable HEDM.

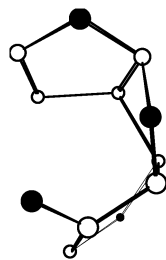


Figure 11. Isomer A with NO_3 and NN_3 bonds broken. This is the intermediate after two steps of the dissociation path for isomer A (nitrogen atoms in white, oxygen atoms in black).

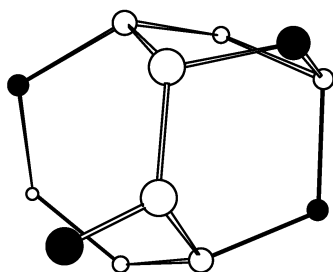


Figure 12. Isomer B with NO_2 and NN_5 bonds broken. This is the intermediate after two steps of the dissociation path for isomer B (nitrogen atoms in white, oxygen atoms in black).

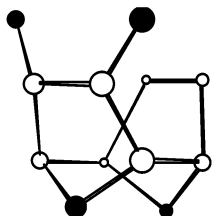


Figure 13. Isomer C with two NO bonds broken. This is the intermediate after two steps of the dissociation path for isomer C (nitrogen atoms in white, oxygen atoms in black).

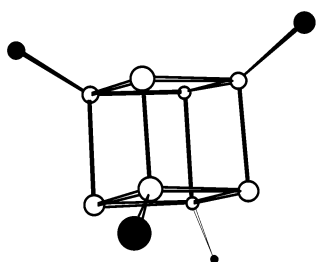


Figure 14. N_8O_4 'exo' isomer. The molecule has T_d point group symmetry (nitrogen atoms in white, oxygen atoms in black).

Finally, there exists an N_8O_4 isomer that is a three-dimensional analogue to a planar N_6O_3 that has been reported¹⁹ as a stable molecule. The N_6O_3 ring has oxygens coordinate-bonded to the exterior of the ring at alternating nitrogens, the idea being that the oxygens would create partial positive charges on every second nitrogen, polarize the $N-N$ bonds, and stabilize the ring. Figure 14 shows an N_8O_4 cage designed around the same basic idea. Four oxygens are coordinate-bonded to the exterior of an N_8 cube at alternating positions. Every nitrogen with oxygen is bonded to three nitrogens without oxygen, and vice versa. This "exo" N_8O_4 was optimized at the HF/CC-PVDZ and MP3/CC-PVDZ level of theory, resulting in energies of +147.2 and +101.9 kcal/mol, respectively, relative to isomer

A. The "exo" oxygenation pattern leaves all six four-membered nitrogen rings intact, resulting in an unstable isomer that is probably not a viable HEDM.

Conclusion

Oxygen insertion into four $N-N$ bonds of an N_8 cube results in cage isomers of N_8O_4 that still have all single bonds ($N-N$ and $N-O$). The most thermodynamically stable N_8O_4 cages are the ones in which all six four-membered rings of the cube have at least one inserted oxygen atom. Three such isomers with zero intact four-membered rings have been studied to determine their resistance to bond breaking. In contrast to the recently studied N_8O_6 , the isomers of N_8O_4 all have been shown to have at least one dissociation pathway with energies below the suggested 30 kcal/mol threshold for a viable HEDM. Six oxygen atoms are sufficient to stabilize the N_8 cube, but four oxygen atoms are not enough.

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