J. Phys. Chem. A 2006, 110, 13889−13894

Isomer Stability and Bond-Breaking Energies of $N_8C_8H_8$ Cages

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Received: September 15, 2006; In Final Form: November 2, 2006

Molecules consisting entirely or predominantly of nitrogen have been extensively investigated for their potential as high-energy density materials (HEDM). Such molecules react to produce N_2 and large amounts of energy, but many such molecules are too unstable for practical applications. In the present study, cage isomers of $N_8C_8H_8$ are studied using theoretical calculations to determine the structural features that lead to the most stable cages and determine the energetics of dissociation for the various isomers. The isomers are evaluated for thermodynamic (isomer vs isomer) stability and kinetic (with respect to dissociation) stability. Density functional theory (B3LYP), perturbation theory (MP2), and coupled-cluster theory [CCSD(T)] are employed, in conjunction with the cc-pVDZ basis set of Dunning. Trends in isomer stability and dissociation energies are calculated and discussed.

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[1,14,15] 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 molecules and polyazides[18,19] of atoms and molecules, such as 1,3,5-triazine. Future developments in experiment and theory will further broaden the horizons of high-energy nitrogen research.

The stability properties of N_x molecules have also been extensively studied in a computational survey[20] of various structural forms with up to 20 atoms. Cyclic, acyclic, and cage isomers have been examined to determine the bonding properties and energetics over a wide range of molecules. A more recent computational study[21] of cage isomers of N_{12} examined the specific structural features that lead to the most stable molecules among the three-coordinate nitrogen cages. Those results showed that molecules with the most pentagons in the nitrogen network tend to be the most stable, with a secondary stabilizing effect due to triangles in the cage structure. A recent study[22] of larger nitrogen molecules N_{24}, N_{30}, and N_{36} showed significant deviations from the pentagon-favoring trend. Each of these molecule sizes has fullerene-like cages consisting solely of pentagons and hexagons, but a large stability advantage was found for molecules with fewer pentagons, more triangles, and an overall structure more cylindrical than spheroidal. Studies[23,24] of intermediate-sized molecules N_{14}, N_{16}, and N_{18} also showed that the cage isomer with the most pentagons was not the most stable cage, even when compared to isomer(s) containing triangles (which have 60° angles that should have significant angle strain). For each of these molecule sizes, spheroidally shaped molecules proved to be less stable than elongated, cylindrical ones.

However, while it is possible to identify in relative terms which nitrogen cages are the most stable, it has been shown[7] in the case of N_{12} that even the most stable N_{12} cage is unstable with respect to dissociation. The number of studies demonstrating the instability of various all-nitrogen molecules has resulted in considerable attention toward compounds that are predominantly nitrogen but contain heteroatoms that stabilize the structure. In addition to the experimental studies[16−18] cited above, theoretical studies have been carried out that show, for example, that nitrogen cages can be stabilized by oxygen insertion[25,26] or phosphorus substitution.[27]

A study[28] of carbon−nitrogen cages showed that carbon substitution into an N_{12} cage results in a stable $N_6C_6H_6$, but the only isomer considered was one in which the six carbon atoms replaced the nitrogen atoms in the two axial triangles of the original N_{12}. A further study[29] of several isomers of $N_6C_6H_6$ showed that, for substitutions of carbon atoms into an N_{12} cage, the most stable isomers were the ones with the largest number of C−N bonds. Also, the isomers with the highest number of C−N bonds also had the highest dissociation energies in the N−N bonds, which is significant because the N−N were weaker than other bonds in the cage. The strength of the N−N bonds, therefore, plays a key role in the overall stability of the molecules with respect to dissociation.

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10.1021/jp066032b CCC: $33.50

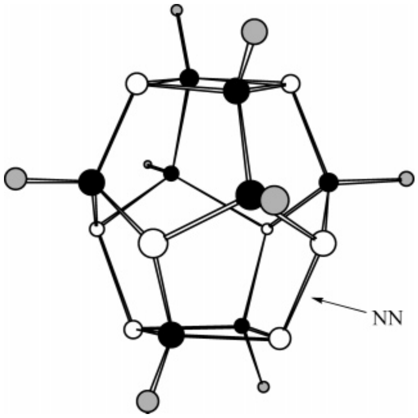

Figure 1. $N_8C_8H_8$ cage isomer 4A (symmetry point group C_2). Nitrogen atoms are shown in white, carbon atoms in black, and hydrogen atoms in gray. Symmetry-independent nitrogen−nitrogen bonds are labeled.

In the present study, a set of isomers of $N_8C_8H_8$ is studied by theoretical calculations to determine trends of isomer stability as well as trends in the dissociation energies of the N−N bonds. These isomers are based on a previously studied N_{16} cage, namely, the "0280" cage, which consists entirely of four- and five-membered rings and should therefore be less affected by ring strain considerations than the previously studied $N_6C_6H_6$ cages. A wide range of isomers, 18 in all, is examined to determine the energetic consequences of various arrangements of the carbon atoms in the cage. Thermodynamic stability is determined by energetic comparisons among the various isomers. Kinetic stability is determined from dissociation energies of the N−N bonds in the cages, and the factors that contribute to stabilizing the N−N bonds are analyzed and discussed.

Computational Methods

Geometries are optimized with density functional theory[30,31] (B3LYP) and second-order perturbation theory[32] (MP2). Single energy points are calculated with coupled-cluster theory[33] [CCSD(T)]. Molecules are optimized in the singlet state, and dissociation intermediates are optimized in the triplet state, which is the ground state for all dissociations in this study. The basis set is the polarized valence double-ζ (cc-pVDZ) set of Dunning.[34] The Gaussian03 computational chemistry software[35] (along with Windows counterpart Gaussian03W) has been used for all calculations in this study.

Results and Discussion

The 18 square-pentagon isomers of $N_8C_8H_8$ are shown in Figures 1−18. The isomers are all based on the same structural framework, differing from one another only in the placement of the carbon (and hydrogen) atoms. For nomenclature purposes, each isomer has a numerical name based on the number of carbon atoms occupying the two squares in the structure. For example, the isomer with all eight carbon atoms in the squares is called "isomer 8". (This isomer, in fact, appeared in a previous study[36] of 4-fold-symmetric carbon−nitrogen cages.) Two or more isomers with the same number of carbon atoms in the squares are distinguished by alphabetic labels and are referred to as, for example, isomer 4A, isomer 4B, and so on. Each isomer is shown with labels on the symmetry-independent nitrogen−nitrogen bonds.

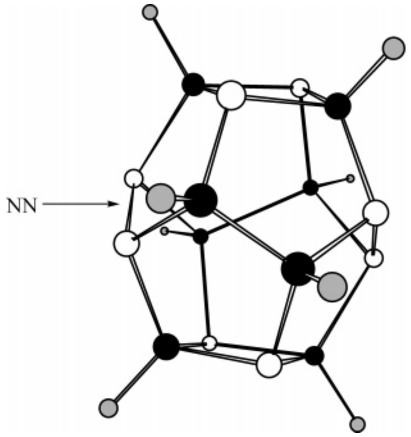

Figure 2. $N_8C_8H_8$ cage isomer 4C (symmetry point group D_2), displayed as described for Figure 1.

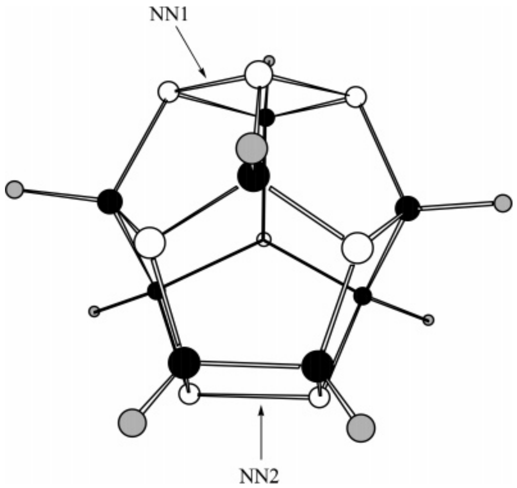

Figure 3. $N_8C_8H_8$ cage isomer 3A (symmetry point group C_s), displayed as described for Figure 1.

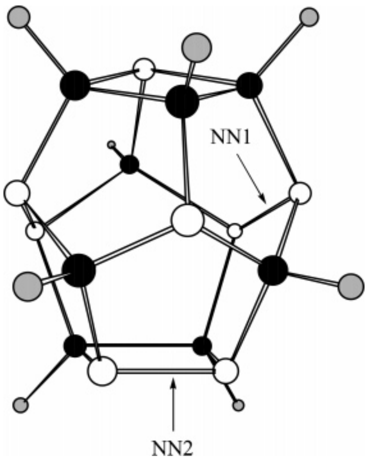

Figure 4. $N_8C_8H_8$ cage isomer 5 (symmetry point group C_s), displayed as described for Figure 1.

The geometries of all 18 isomers have been optimized with B3LYP/cc-pVDZ theory and MP2/cc-pVDZ theory, with CCSD(T)/cc-pVDZ energies computed at the MP2/cc-pVDZ theory level. The relative energies of the 18 isomers are shown in Table 1. The energies of each isomer are tabulated along with bonding information about the number of carbon−carbon, carbon−nitrogen, and nitrogen−nitrogen bonds in the framework; in all cases the framework has a total of 24 bonds. The data in Table 1 demonstrate first and foremost that thermodynamic stability is conferred by C−N bonds relative to C−C and N−N bonds. The most stable isomers also have the largest number of C−N bonds. This is straightforwardly explained by bond strength, since C−C, C−N, and N−N bonds have bond

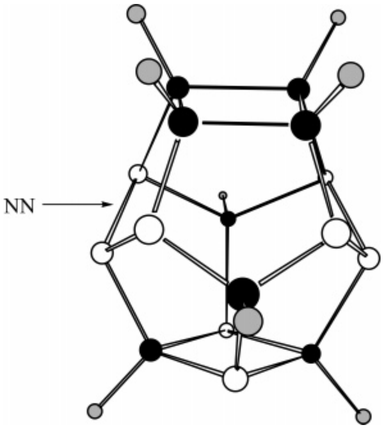

Figure 5. $N_8C_8H_8$ cage isomer 6C (symmetry point group C_{2v}), displayed as described for Figure 1.

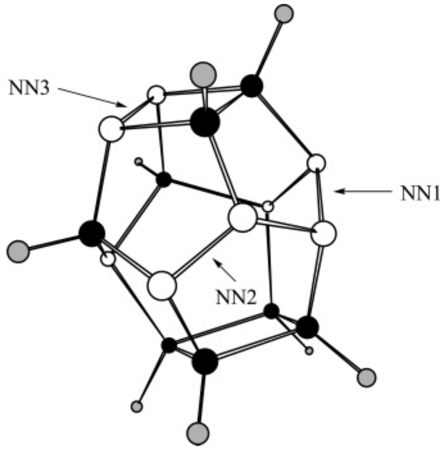

Figure 6. $N_8C_8H_8$ cage isomer 6D (symmetry point group C_s), displayed as described for Figure 1.

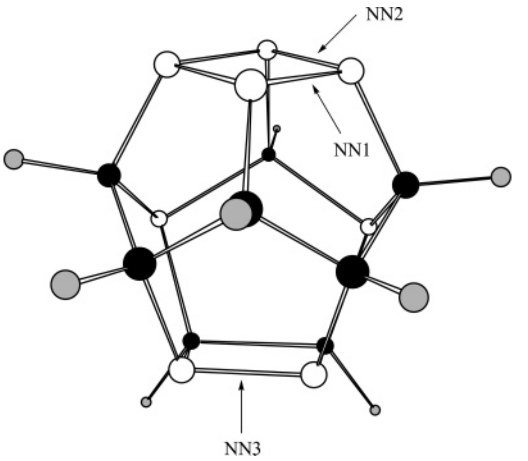

Figure 7. $N_8C_8H_8$ cage isomer 2B (symmetry point group C_s), displayed as described for Figure 1.

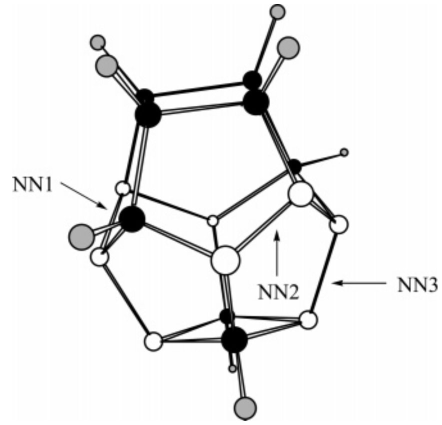

Figure 8. $N_8C_8H_8$ cage isomer 6B (symmetry point group C_2), displayed as described for Figure 1.

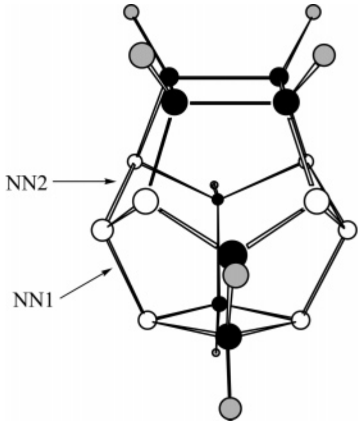

Figure 9. $N_8C_8H_8$ cage isomer 6A (symmetry point group C_{2v}), displayed as described for Figure 1.

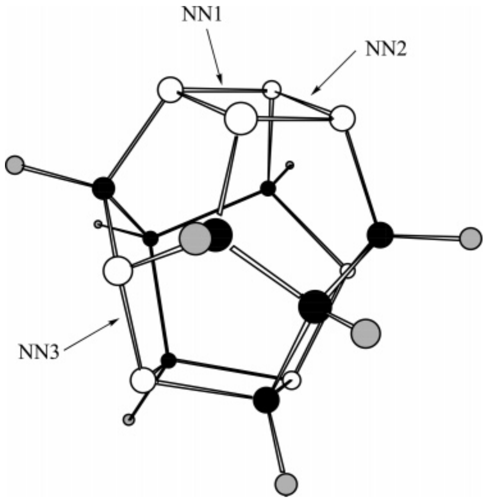

Figure 10. $N_8C_8H_8$ cage isomer 2A (symmetry point group C_{2v}), displayed as described for Figure 1.

enthalpies[37] of 83.2, 72.9, and 39.0 kcal/mol, respectively. Replacement of C−C and N−N bonds by a pair of C−N bonds should stabilize the molecule by 23.6 kcal/mol. The actual calculations from Table 1 suggest a stabilization of 15−20 kcal/mol per pair of additional C−N bonds.

It should be noted, however, that further stabilization of $N_8C_8H_8$ by reducing the number of homonuclear framework bonds to zero is not possible. A structure in which all 24 framework bonds were C−N bonds would have many more four-membered rings and be subject to severe ring strain effects. Such a structure is shown in Figure 19. Calculations on this isomer, which is based on a different framework than the other molecules in this study, indicate that the molecule has energy of +50.3 kcal/mol with B3LYP/cc-pVDZ theory and +53.5 kcal/mol with MP2/cc-pVDZ theory, with respect to isomer 4A. The molecule in Figure 19 is therefore less stable than several molecules from Table 1, despite having 24 carbon−nitrogen bonds.

The bond enthalpy data also indicate that the N−N bonds should be the weakest bonds in each molecule, a conclusion supported by previous calculations[29] on $N_6C_6H_6$ molecules. This means that the kinetic stability of the isomers is determined by

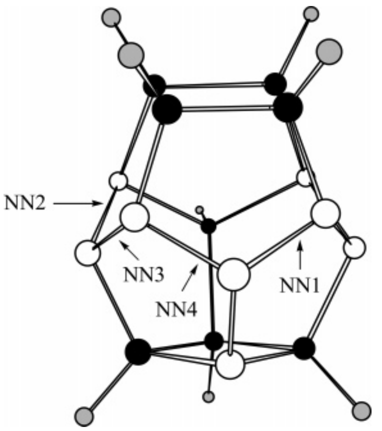

Figure 11. $N_8C_8H_8$ cage isomer 7 (symmetry point group C_s), displayed as described for Figure 1.

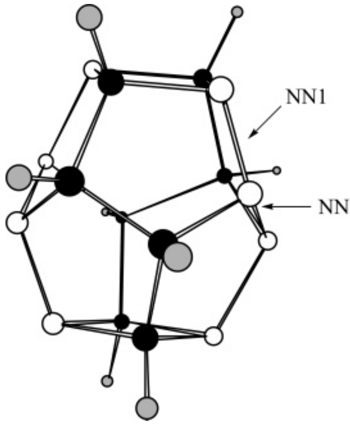

Figure 12. $N_8C_8H_8$ cage isomer 4D (symmetry point group D_2), displayed as described for Figure 1.

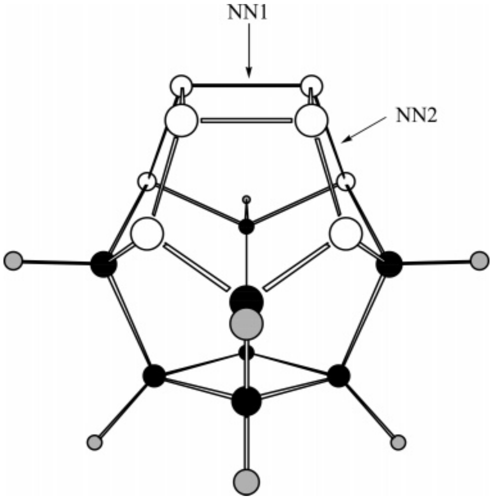

Figure 13. $N_8C_8H_8$ cage isomer 4B (symmetry point group C_{4v}), displayed as described for Figure 1.

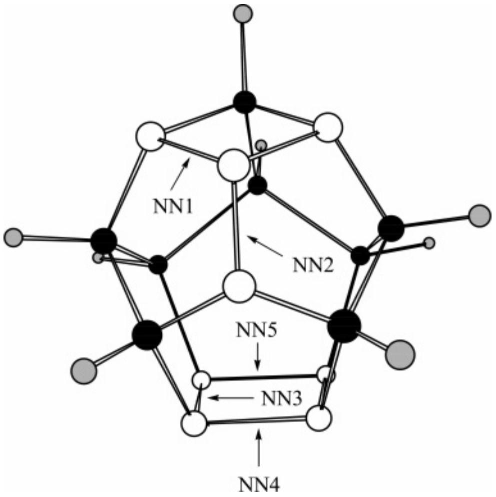

Figure 14. $N_8C_8H_8$ cage isomer 1 (symmetry point group C_s), displayed as described for Figure 1.

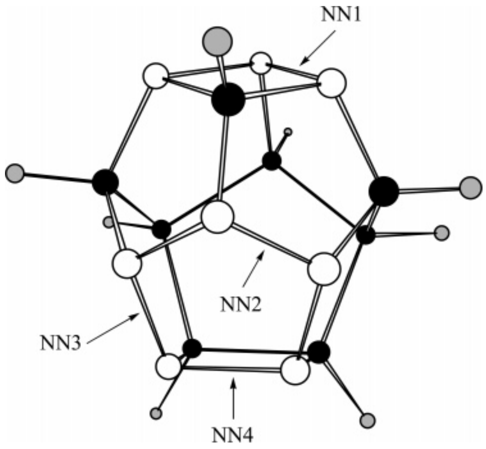

Figure 15. $N_8C_8H_8$ cage isomer 3B (symmetry point group C_s), displayed as described for Figure 1.

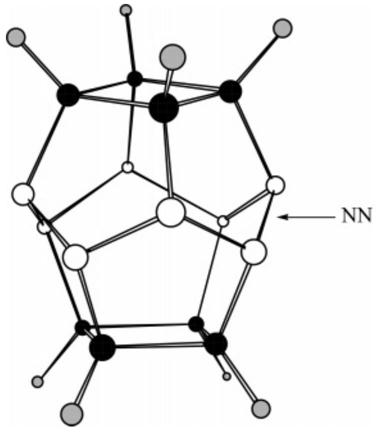

Figure 16. $N_8C_8H_8$ cage isomer 8 (symmetry point group D_{4d}), displayed as described for Figure 1.

the dissociation characteristics of the N−N bonds. Dissociation energies for N−N bonds for all the molecules in this study have been calculated with MP2/cc-pVDZ and tabulated in Table 2 as the difference in energy between the intact isomer and the intermediate with one N−N bond broken. The N−N dissociation energies exhibit wide variations, with some bonds dissociating at 39−40 kcal/mol and others requiring 70−80 kcal/mol to dissociate. (Available computational resources are insufficient for CCSD(T)/cc-pVDZ dissociation energies, but previous experience[29] suggests that the results would be 10−15 kcal/mol less than the MP2 values.) For the purposes of investigating the variations in N−N bond strength, the N−N bonds in these molecules are classified into the following categories: class A, nitrogen−nitrogen bonds in which both atoms belong to a four-membered ring; class B, nitrogen−nitrogen bonds in which one atom belongs to a four-membered ring; and class C, nitrogen−nitrogen bonds in which neither atom belongs to a four-membered ring.

This classification scheme is shown in Table 2. The nitrogen−nitrogen bonds are further classified by their bonding environ-

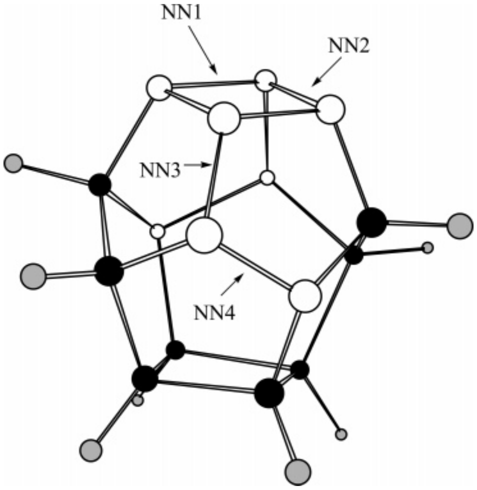

Figure 17. $N_8C_8H_8$ cage isomer 4E (symmetry point group C_2), displayed as described for Figure 1.

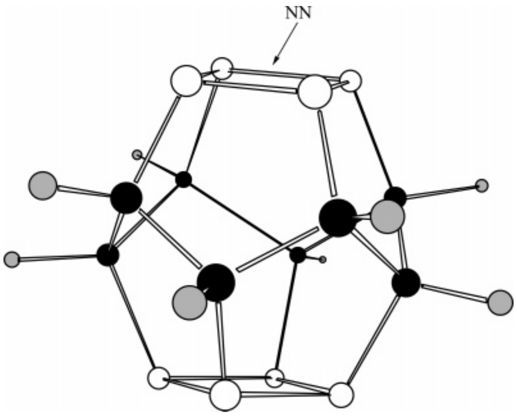

Figure 18. $N_8C_8H_8$ cage isomer 0 (symmetry point group D_{4d}), displayed as described for Figure 1.

TABLE 1: Relative Energies of $N_8C_8H_8$ Isomers[a]

	energy (kcal/mol)			
isomer	CC/CN/NN bonds	B3LYP	MP2	CCSD(T)//MP2
4A	2/20/2	0.0	0.0	0.0
4C	2/20/2	+2.6	+3.7	+3.7
3A	3/18/3	+16.5	+18.9	+17.4
5	3/18/3	+17.2	+19.7	+18.8
6C	4/16/4	+31.5	+35.4	+33.8
6D	5/14/5	+45.7	+50.7	+48.5
2B	5/14/5	+48.7	+53.7	+49.9
6B	6/12/6	+65.3	+70.7	+67.9
6A	6/12/6	+66.8	+73.0	+69.8
2A	6/12/6	+69.1	+75.0	+70.5
7	7/10/7	+74.4	+80.9	+77.9
4D	6/12/6	+75.7	+82.5	+78.2
4B	8/8/8	+79.7	+83.9	+80.4
1	7/10/7	+78.9	+85.5	+80.0
3B	7/10/7	+80.9	+87.1	+82.6
8	8/8/8	+87.6	+96.3	+92.7
4E	8/8/8	+94.3	+102.0	+96.7
0	8/8/8	+96.6	+105.0	+98.2

[a] Calculated with CC-pVDZ basis set. For each molecule, the numbers of C−C, C−N, and N−N bonds are also shown.

ment. Each nitrogen−nitrogen bond has an environment of four other bonds (each of the nitrogens is involved in two other bonds). These four neighbor bonds are either C−N or N−N bonds. Table 2 shows the number of neighboring C−N bonds for each N−N bond. (Four bonds are missing from Table 2 because of failed optimizations of the intermediates: NN1 and NN2 of isomer 4B and NN1 and NN2 of isomer 4E.)

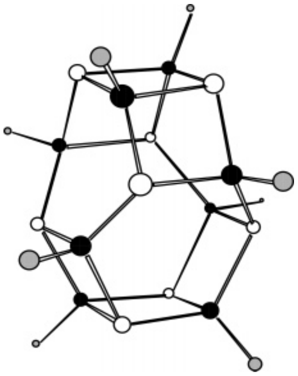

Figure 19. $N_8C_8H_8$ cage isomer in which all framework bonds are C−N bonds (symmetry point group S_4). This isomer has more C−N bonds than the other isomers in this study but suffers from ring strain in the additional four-membered rings.

TABLE 2: Nitrogen−Nitrogen Bond Dissociation Energies for $N_8C_8H_8$ Cages[a]

bond class	C−N neighbors	molecule	bond	MP2 energy (kcal/mol)
A	2	2B	NN1	42.5
		2B	NN2	47.6
		2A	NN1	40.3
		2A	NN2	49.9
		1	NN1	39.2
		1	NN3	41.3
		1	NN4	47.7
		1	NN5	45.1
		3B	NN4	47.6
		0	NN	43.1
A	3	3A	NN1	45.8
		3B	NN1	42.7
A	4	3A	NN2	50.5
		6D	NN3	51.4
		5	NN2	50.6
		2B	NN3	44.7
B	1	4E	NN3	57.6
B	2	6A	NN1	55.7
		7	NN1	80.5
		1	NN2	66.8
		3B	NN3	72.5
B	3	6B	NN3	69.4
		4D	NN1	55.7
B	4	4A	NN	78.3
		2A	NN3	67.5
C	1	7	NN4	41.7
C	2	6D	NN1	43.2
		6B	NN1	48.4
		6A	NN2	50.8
		7	NN3	48.2
		3B	NN2	50.3
		4D	NN2	47.8
		8	NN	44.4
C	3	6C	NN	56.3
		6D	NN2	56.2
		6B	NN2	58.5
		7	NN2	55.1
		4E	NN4	59.9
C	4	4C	NN	72.9
		5	NN1	71.7

[a] Energies were calculated with MP2/cc-pVDZ theory. Bond labels correspond to Figures 1−18. The classification scheme for the N−N bonds is described in the text.

Class A nitrogen−nitrogen bonds have MP2/cc-pVDZ bond dissociation energies of 40−50 kcal/mol regardless of the nature of the bonding environment. No strong environmental effects are shown by these bonds. Since these bonds belong to a four-membered ring, it is likely that ring strain is the major factor determining the bond strengths. Class B nitrogen−nitrogen bonds show a larger variation of bond energies (from 55 to 80 kcal/mol), but they also do not show any strong dependencies on the bonding environment. Class B bonds are stronger than class A bonds because ring strain is not a consideration for class B bonds, since class B bonds are edges shared between pentagons, which should be nearly strain-free.

Table 2 shows that class C bonds demonstrate a strong dependence on the environment of neighboring bonds. If a class C bond has only one or two C−N bonds in the bonding environment, the MP2/cc-pVDZ bond energy is 40−50 kcal/mol, about the same as a class A bond. Class C bonds with three C−N bond neighbors have an MP2/cc-pVDZ dissociation energy between 55 and 60 kcal/mol, and bonds with four C−N bond neighbors have dissociation energy above 70 kcal/mol. Since the class C bonds are farthest from the four-membered rings, they are the least susceptible to ring strain effects. Therefore, class C bonds are most affected by the bonding environment. The presence of C−N bonds around an N−N bond appears to structurally reinforce the N−N bond and make it stronger and, therefore, less susceptible to dissociation.

Conclusion

A variety of $N_8C_8H_8$ cage isomers, based on a framework with two four-membered rings and eight pentagons, have been studied. Arranging the atoms so as to maximize the number of C−N bonds leads to the most stable isomers, but changing the framework to maximize the number of C−N bonds does not lead to enhanced stability. Nitrogen−nitrogen bonds, as the weakest bonds in the molecule, determine the stability of the molecule as a whole, but the strength of the N−N bonds is strongly dependent on the bond's position within the molecule and/or the environment in which the N−N bond is located. The results of this study provide design principles that may lead to stable structures of even larger high-energy carbon−nitrogen cages.

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 CHE050022N and utilized the IBM p690 cluster in Champaign, IL. R.C., J.J., A.G., and D.S. are undergraduate scholars 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 supported by the National Science Foundation (NSF/HBCU-UP Grant 0505872). D.M. is supported by NSF/HBCU-UP as an undergraduate scholar. This work was also supported by the National Institutes of Health (NIH/NCMHD 1P20MD000547-01). This work is also supported by the Petroleum Research Fund, administered by the American Chemical Society (PRF grant 43798-B6). The taxpayers of the state of Alabama in particular and the United States in general are gratefully acknowledged.

Supporting Information Available: Tables showing the optimized geometries of the isomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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