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Stability of Carbon−Nitrogen Cages in Fourfold Symmetry

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Molecules consisting entirely of nitrogen have been studied extensively for their potential as high-energy density materials (HEDM). Many nitrogen molecules previously studied have low-energy dissociation routes and are therefore too unstable to serve as practical HEDM. However, the incorporation of heteroatoms into a nitrogen structure can have stabilizing effects. Theoretical calculations are carried out on a sequence of high-energy cages with carbon and nitrogen. Density functional theory (B3LYP), perturbation theory (MP2 and MP4), and coupled-cluster theory (CCSD(T)) are used in conjunction with the correlation-consistent basis sets of Dunning. Stability trends as a function of molecule size 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 to 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 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 stability properties of N_x molecules have also been extensively studied in a computational survey[19] 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[20] 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[21] 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[22,23] 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[24,25] or phosphorus substitution.[26]

A study[27] of carbon−nitrogen cages showed that carbon substitution into an N_{12} cage results in a stable $N_6C_6H_6$, but larger, nitrogen-richer molecules were predicted to be less stable than $N_6C_6H_6$. Replacement of the nitrogen triangles in N_{12} by carbon triangles led to the stable $N_6C_6H_6$, but it is possible that angle strain in the triangles still influenced the stability of the molecules. In the current study, carbon−nitrogen cages are examined in 4-fold symmetry rather than 3-fold, with carbon squares rather than triangles. Starting with a cage $N_8C_8H_8$, a 4-fold-symmetric counterpart to $N_6C_6H_6$, a sequence of molecules will be tested to determine if this further relief of ring strain enhances the stability of the molecules. The stability of each carbon−nitrogen cage is determined by theoretical calculations of the energies of various dissociation pathways.

Computational Details

Geometries are optimized with density functional theory[28,29] (B3LYP) and second-order perturbation theory[30] (MP2). Single energy points are calculated with fourth-order perturbation theory[30] (MP4(SDQ)) and coupled-cluster theory[31] (CCSD(T)). Molecules are optimized in the singlet state, and dissociation intermediates are optimized in the triplet state, which is the

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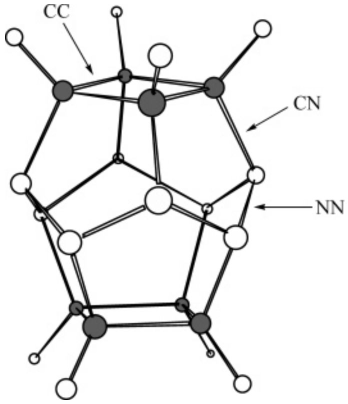

Figure 1. $N_8C_8H_8$ molecule, with three symmetry-independent bonds labeled. The molecule has D_{4d} point group symmetry. Nitrogen atoms are shown in white, carbon atoms are in gray, and hydrogen atoms are in white on the ends of the molecule.

TABLE 1: Bond Dissociation Energies for the $N_8C_8H_8$ Cage[a]

energy	geometry	CC	CN	NN
		bonds (see Figure 1)		
B3LYP/cc-pVDZ	B3LYP/cc-pVDZ	+65.8	+72.9	+25.0
MP2/cc-pVDZ	MP2/cc-pVDZ	+78.1	+92.3	+44.4
MP2(+ZPE)/cc-pVDZ	MP2/cc-pVDZ	+75.5	+89.7	+43.7
MP4/cc-pVDZ	MP2/cc-pVDZ	+72.3	+83.6	+35.5
CCSD(T)/cc-pVDZ	MP2/cc-pVDZ	+71.0	+80.3	+34.2
MP2/aug-cc-pVDZ	MP2/aug-cc-pVDZ	+78.2	+93.5	+46.8
MP2/cc-pVTZ	MP2/cc-pVTZ	+80.0	+95.5	+46.8
MP4/aug-cc-pVDZ	MP2/aug-cc-pVDZ	+72.3	+84.4	+37.4

[a] Energies in kcal/mol.

ground state for all dissociations in this study. [Open-shell calculations have been carried out using UHF. Spin contamination is not a significant problem. For example, for the MP2/cc-pVDZ calculations on the three intermediates of $N_8C_8H_8$, the S^2 values are all between 2.03 and 2.06.] Vibrational frequencies have been calculated at the MP2/cc-pVDZ level of theory for $N_8C_8H_8$ and its dissociation intermediates. B3LYP/cc-pVDZ frequencies have been calculated for all intact molecules in this study. The basis sets are the double-ζ (cc-pVDZ), augmented double-ζ (aug-cc-pVDZ), and triple-ζ (cc-pVTZ) sets of Dunning.[32] The Gaussian03 computational chemistry software[33] has been used for all calculations in this study.

Results and Discussion

$N_8C_8H_8$. The smallest molecule in this study is the $N_8C_8H_8$ molecule shown in Figure 1. The molecule has D_{4d} point group symmetry and three symmetry-independent bonds. The bond dissociation energies for these bonds have been tabulated in Table 1. As with the previously studied $N_6C_6H_6$, the NN bond is the weakest, but its dissociation energy is over 30 kcal/mol at the CCSD(T)/cc-pVDZ level of theory, which should be considered the most reliable calculation in Table 1. Basis set effects, calculated with MP2 theory, indicate that larger basis sets increase the bond-breaking energies slightly. Inclusion of zero-point energy decreases the bond energies, but the decrease is less than the increasing effect of the larger basis sets for the NN bond. Therefore, the actual dissociation energy for the NN bond is most likely even higher than the best cc-pVDZ calculations would indicate. The other bonds have even higher energies, so the $N_8C_8H_8$ molecule should resist dissociation well enough to be a stable high-energy density material.

Larger Molecules. Since it is the nitrogen content of the molecules that provides the energy release, it is favorable to study molecules richer in nitrogen than the $N_8C_8H_8$, which is only 52% nitrogen by mass. The basic design of the $N_8C_8H_8$ has been extended to the larger molecules $N_{16}C_{12}H_8$ and $N_{24}C_{16}H_8$. These larger molecules are shown in Figures 2 and 3 and are composed of 60% and 63% nitrogen by mass, respectively. However, in the 3-fold symmetry study, lengthening the molecule resulted in decreasing stability. Are these larger 4-fold symmetric molecules as stable as the smaller $N_8C_8H_8$? Bond-breaking energies for symmetry-independent bonds (five in $N_{16}C_{12}H_8$ and seven in $N_{24}C_{16}H_8$) are tabulated in Tables 2 and 3. For these molecules, as with $N_8C_8H_8$, the weakest bonds are the N−N bonds. However, the bond-breaking energies are about the same as for $N_8C_8H_8$. The stability of these 4-fold symmetric molecules is not dependent on molecule size, which stands in contrast with the previously studied 3-fold symmetric molecules. The molecules in the current study are all stable enough to serve as HEDM.

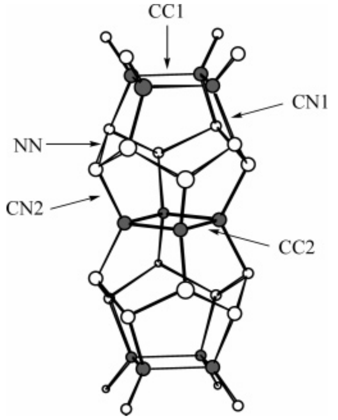

Figure 2. $N_{16}C_{12}H_8$ molecule, with five symmetry-independent bonds labeled. The molecule has D_{4h} point group symmetry. Nitrogen atoms are shown in white, carbon atoms are in gray, and hydrogen atoms are in white on the ends of the molecule.

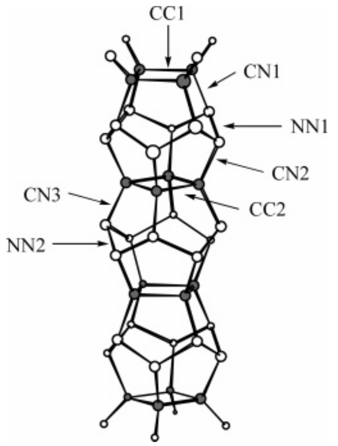

Figure 3. $N_{24}C_{16}H_8$ molecule, with seven symmetry-independent bonds labeled. The molecule has D_{4d} point group symmetry. Nitrogen atoms are shown in white, carbon atoms are in gray, and hydrogen atoms are in white on the ends of the molecule.

Comparison to Azido Compounds. Although these results indicate the possibility of an entire class of stable high-energy molecules, the general stoichiometry of these molecules in the limit of large sizes is N_2C. This means the class of 4-fold symmetric molecules has a theoretical upper limit of 70% nitrogen by mass. As stated previously, much research effort is focused on the development of high-energy azido or polyazido compounds, some of which have nitrogen composition well above 70%. The azido functionality is a straightforward way

TABLE 2: Bond Dissociation Energies for the $N_{16}C_{12}H_8$ Cage[a]

energy	geometry	bonds (see Figure 5) CC1	CN1	NN	CN2	CC2
B3LYP/cc-pVDZ	B3LYP/cc-pVDZ	*b*	*b*	+25.5	*b*	+72.8
MP2/cc-pVDZ	MP2/cc-pVDZ	+79.2	+96.6	+45.3	+109.8	+92.3
MP4/cc-pVDZ	MP2/cc-pVDZ	+73.2	+87.1	*c*	+101.1	+84.7

[a] Energies in kcal/mol. [b] Geometry optimization not successful. [c] Calculation exceeds resources, due to C_1 symmetry of intermediate.

TABLE 3: Bond Dissociation Energies for the $N_{24}C_{16}H_8$[a]

bonds (see Figure 6)	B3LYP/cc-pVDZ	MP2/cc-pVDZ
CC1	*b*	+79.2
CN1	*b*	+96.7
NN1	+25.6	+45.1
CN2	*b*	+108.2
CC2	+72.6	+92.5
CN3	*b*	+114.7
NN2	+25.1	+45.1

[a] Energies in kcal/mol. [b] Geometry optimization not successful.

TABLE 4: Free Energies of Unimolecular Dissociation of the Compounds in This Study, with Triazidomethane (N_9CH) Included for Comparison[a]

molecule	% N	reaction	kcal/mol	kcal/g
$N_8C_8H_8$	52	$N_8C_8H_8 \rightarrow 4N_2 + {}^4/_3C_6H_6$	−339.6	−1.6
$N_{16}C_{12}H_8$	60	$N_{16}C_{12}H_8 \rightarrow 8N_2 + {}^2/_3C_6H_6 + {}^1/_3C_{24}H_{12}$	−683.0	−1.8
$N_{24}C_{16}H_8$	63	$N_{24}C_{16}H_8 \rightarrow 12N_2 + {}^2/_3C_{24}H_{12}$	−1028.6	−1.9
N_9CH	91	$N_9CH \rightarrow {}^9/_2N_2 + {}^1/_6C_6H_6$	−243.3	−1.8

[a] Energies calculated using B3LYP/cc-pVDZ method. Mass percentages of nitrogen are shown for each molecule. Benzene (C_6H_6) and coronene ($C_{24}H_{12}$) are graphitic products that are chosen to account for carbon and hydrogen in the decomposition.

TABLE 5: Free Energies of Dissociation of the Compounds in This Study, with Triazidomethane (N_9CH) Included for Comparison[a]

molecule	% N	reaction	kcal/mol	kcal/g
$N_8C_8H_8$	52	$N_8C_8H_8 + 10O_2 \rightarrow 4N_2 + 8CO_2 + 4H_2O$	−1644.2	−7.6
$N_{16}C_{12}H_8$	60	$N_{16}C_{12}H_8 + 14O_2 \rightarrow 8N_2 + 12CO_2 + 4H_2O$	−2514.1	−6.7
$N_{24}C_{16}H_8$	63	$N_{24}C_{16}H_8 + 18O_2 \rightarrow 12N_2 + 16CO_2 + 4H_2O$	−3386.3	−6.3
N_9CH	91	$N_9CH + {}^5/_4O_2 \rightarrow {}^9/_2N_2 + CO_2 + {}^1/_2H_2O$	−406.4	−2.9

[a] The presence of an oxygen atmosphere is assumed. Energies calculated using B3LYP/cc-pVDZ method. Mass percentages of nitrogen are shown for each molecule.

to enrich a molecular structure with nitrogen. It is therefore reasonable to ask how the molecules in Figures 1−3 compare with azido compounds in terms of energy release. Table 4 shows the energy release data for unimolecular dissociation of the three molecules in this study along with an appropriate azido compound for reference, namely, triazidomethane (N_9CH). [Note: For unimolecular dissociation, it is assumed that the carbon becomes graphitic in nature. Graphitic compounds, namely benzene (C_6H_6) and coronene ($C_{24}H_{12}$) are chosen as products.] Triazidomethane is 91% nitrogen by mass, far richer than any molecule in this study, but it is no more energetic than $N_{16}C_{12}H_8$ or $N_{24}C_{16}H_8$, which are both less than 65% nitrogen. The reason for this is a straightforward comparison between the N−N single bonds in the molecules in the current study and the N═N double bonds in the N═N═N azido bonding group, which release less energy[34] upon conversion to the triple bonds in molecular N_2. Therefore, the molecules in this study have energy release properties comparable even to other high-energy molecules that are richer in nitrogen.

Table 5 shows the results of a similar energetic comparison, the difference being the assumption of an oxygen atmosphere. Such an atmosphere would permit not only the decomposition of the nitrogen into N_2 but also combustion of the hydrocarbon content. The energies in Table 5, therefore, include the energies from Table 4 and an additional contribution from the carbon. Not surprisingly, the data in Table 5 vary strongly by the carbon content of each molecule. The triazidomethane had the smallest hydrocarbon contribution to the energy because it has the smallest percentage of hydrocarbon content. The energies of the 4-fold symmetric molecules in this study decrease with increasing size because of decreasing hydrocarbon content. In an oxygen atmosphere, the hydrocarbon content of the molecules in this study provide an even greater energy release relative to azido compounds that are richer in nitrogen.

Conclusion

These 4-fold-symmetric molecules represent an entire class of high-energy materials with no significant variations in stability with respect to molecule size. Successive stacking of eight-membered rings of nitrogen with four-membered rings of carbon results in molecules of arbitrary size as well as substantial energy release properties. Also, the conversion of N−N single bonds to triple bonds is sufficiently energetic to overcome the limitations of the N_2C stoichiometry of the molecules in the current study. $N_8C_8H_8$, $N_{16}C_{12}H_8$, and $N_{24}C_{16}H_8$, as well as their larger analogues, all have the ability to serve as HEDM.

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Supporting Information Available: Additional data on $N_8C_8H_8$, $N_{16}C_{12}H_8$, and $N_{24}C_{16}H_8$. This material is available free of charge via the Internet at http://pubs.acs.org.

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