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Isomer Stability of $N_6C_6H_6$ Cages

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Recent theoretical studies have identified carbon−nitrogen cages that are potentially stable high energy density materials (HEDM). One such molecule is an $N_6C_6H_6$ cage in which a six-membered ring of nitrogen is bonded to C_3H_3 triangles on both sides. This molecule is based on the structure of the most stable N_{12} cage, with six carbon atoms substituted into the structure. In the current study, several $N_6C_6H_6$ isomers (including the previously studied cage) are examined by theoretical calculations to determine which is actually the most stable. Stability will be evaluated from two points of view: (1) thermodynamic stability of one isomer versus another and (2) kinetic stability of each isomer as determined by the energetics of bond breaking. Density functional theory (B3LYP), perturbation theory (MP2 and MP4), and coupled-cluster theory (CCSD(T)) are used in this study, along with the correlation-consistent basis sets of Dunning. Trends in thermodynamic and kinetic stability are 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 eight to twelve 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 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, although 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 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}. In the current study, a range of isomers of $N_6C_6H_6$ are studied by theoretical calculations to determine the effects on stability of various other placements of the six carbon atoms. The resulting cage isomers are compared to each other in terms of thermodynamic stability, and the kinetic stability of each isomer is evaluated by calculations of the energies of dissociation processes.

Computational Methods

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

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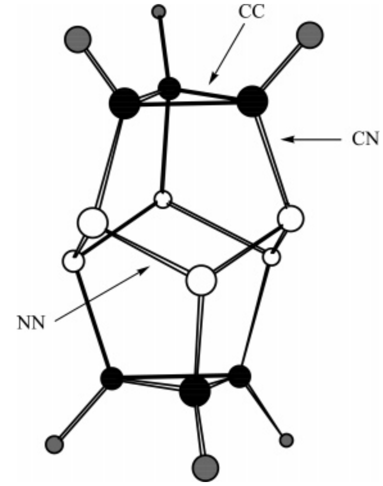

Figure 1. $N_6C_6H_6$ isomer 6. All six carbon atoms lie on the axial triangles, and the molecule has D_{3d} point group symmetry. Nitrogen atoms are shown in white, carbon in black, and hydrogen in gray. Symmetry-independent bonds have been labeled.

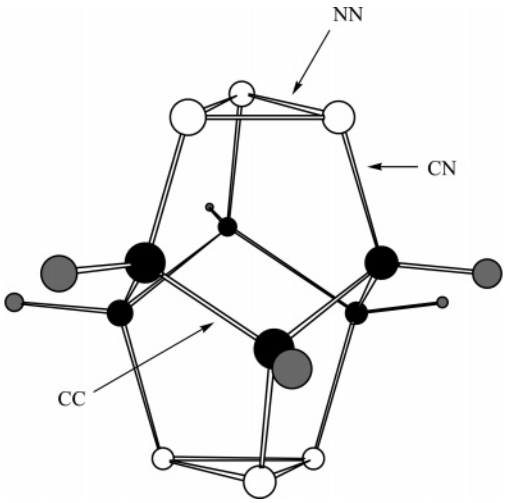

Figure 2. $N_6C_6H_6$ isomer 0. All six carbon atoms lie on the equatorial belt, and the molecule has D_{3d} point group symmetry. Nitrogen atoms are shown in white, carbon in black, and hydrogen in gray. Symmetry-independent bonds have been labeled.

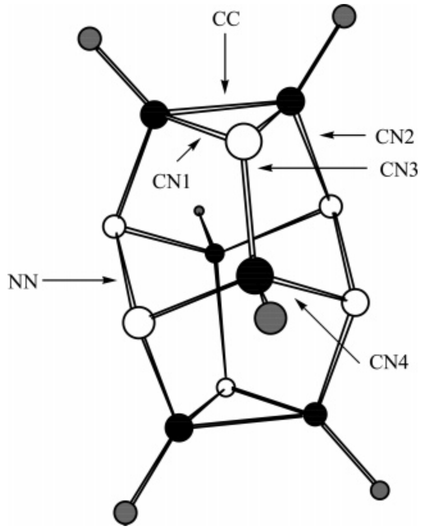

Figure 3. $N_6C_6H_6$ isomer 4. Four carbon atoms lie on the axial triangles, and the molecule has C_{2h} point group symmetry. Nitrogen atoms are shown in white, carbon in black, and hydrogen in gray. Symmetry-independent bonds have been labeled.

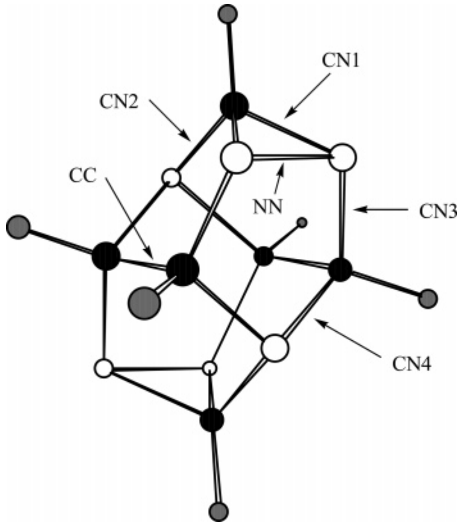

Figure 4. $N_6C_6H_6$ isomer 2. Two carbon atoms lie on the axial triangles, and the molecule has C_{2h} point group symmetry. Nitrogen atoms are shown in white, carbon in black, and hydrogen in gray. Symmetry-independent bonds have been labeled.

intermediates are optimized in the triplet state, which is the ground state for all dissociations 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

Four cage isomers of $N_6C_6H_6$ are under consideration in this study, and they are shown in Figures 1−4, with labels added for symmetry-independent bonds. All the isomers are based on the cage network of the most stable N_{12} cage, which was labeled "2060" in ref 20. The basic framework consists of two axial triangles and an equatorial "belt" of six atoms. Each isomer is named for the number of carbon atoms in the axial triangles. Figure 1, therefore, shows the molecule called isomer 6, because all six carbon atoms occupy the positions on the axial triangles. This isomer was studied in ref 27, and all results in this work relating to isomer 6 are taken from ref 27. Figure 2 shows isomer 0, so named because all six carbons lie on the equatorial belt (zero carbons in axial triangles). Isomer 4 and isomer 2 are shown in Figures 3 and 4, respectively. These four molecules are intended to provide a representative sample of possibilities for arranging the carbon and nitrogen atoms, and these molecules are studied to determine stability properties and potential as HEDM.

Isomer vs Isomer Stability. Table 1 shows the relative energies of the four isomers. The most stable isomers are isomer 4 and isomer 2, and the primary reason is the relative bond strength between C−C, C−N, and N−N bonds. The bond energies[34] for these bonds are 83.2, 72.9, and 39.0 kcal/mol, respectively. Therefore, for any rearrangement of the atoms, the replacement of a C−C and N−N bond with two C−N bonds should be energetically advantageous by 23.6 kcal/mol. Relative to isomer 6 and isomer 0, isomers 4 and 2 should reap the benefit of four such substitutions and should be more stable by about 95 kcal/mol. The actual molecules (isomer 4 and isomer 2) have a stability advantage of 55−65 kcal/mol, somewhat less than expected on the basis of bond energy alone. If two isomers are compared that have the same number of each type bond (comparing isomer 6 vs isomer 0 or isomer 4 vs isomer 2), the

TABLE 1: Bond Properties and Relative Energies of the $N_6C_6H_6$ Isomers (Energies in kcal/mol)

		isomer 6	isomer 0	isomer 4	isomer 2
bonds	C−C bonds	6	6	2	2
	C−N bonds	6	6	14	14
	N−N bonds	6	6	2	2
energies[a]	B3LYP/cc-pVDZ	0.0	−9.5	−53.1	−56.8
	MP2/cc-pVDZ	0.0	−15.3	−58.9	−63.9
	MP4(SDQ)/cc-pVDZ	0.0	−13.7	−58.6	−63.3
	CCSD(T)/cc-pVDZ	0.0	−15.2	−56.4	−61.8
	MP2/aug-cc-pVDZ	0.0	−15.4	−56.8	−62.2
	MP4(SDQ)/aug-cc-pVDZ	0.0	−13.2	−56.8	−61.5
	MP2/cc-pVTZ	0.0	−13.9	−59.0	−63.8
	MP4(SDQ)/cc-pVTZ	0.0	−11.8	−59.3	−63.6

[a] Energies with MP4(SDQ) and CCSD(T) are carried out at MP2 geometries optimized with the same basis set.

TABLE 2: Bond-Breaking Energies for $N_6C_6H_6$ Isomers, Calculated with cc-pVDZ Basis Set (Energies in kcal/mol)[a]

	isomer 6	isomer 0	isomer 4	isomer 2
B3LYP	+68.4 (CC)	n/a (CC)	+63.7 (CC)	n/a (CC)
	+85.8 (CN)	+67.3 (CN)	+60.1 (CN1)	+48.7 (CN1)
	+21.3 (NN)	+25.3 (NN)	+83.1 (CN2)	+87.4 (CN2)
			+97.3 (CN3)	+77.8 (CN3)
			+51.2 (CN4)	n/a (CN4)
			+40.6 (NN)	+37.9 (NN)
MP2	+78.7 (CC)	+96.0 (CC)	+74.8 (CC)	+83.7 (CC)
	+105.5 (CN)	+81.2 (CN)	+74.2 (CN1)	+64.8 (CN1)
	+42.5 (NN)	+45.2 (NN)	+103.5 (CN2)	+102.9 (CN2)
			+114.2 (CN3)	+93.9 (CN3)
			+71.9 (CN4)	+85.9 (CN4)
			+61.7 (NN)	+53.3 (NN)
MP4(SDQ)[b]	+71.3 (CC)	+85.8 (CC)	+67.9 (CC)	+75.8 (CC)
	+96.1 (CN)	+72.5 (CN)	+63.9 (CN1)	+55.2 (CN1)
	+31.8 (NN)	+32.2 (NN)	+94.2 (CN2)	+94.1 (CN2)
			+104.2 (CN3)	+84.9 (CN3)
			+62.6 (CN4)	+74.6 (CN4)
			+49.1 (NN)	+40.1 (NN)
CCSD(T)[b]	+71.4 (CC)	+84.0 (CC)	+67.9 (CC)	+74.7 (CC)
	+93.0 (CN)	+72.2 (CN)	+64.5 (CN1)	+54.7 (CN1)
	+31.4 (NN)	+32.1 (NN)	+91.4 (CN2)	+92.9 (CN2)
			+103.0 (CN3)	+83.9 (CN3)
			+61.8 (CN4)	+72.1 (CN4)
			+48.9 (NN)	+41.8 (NN)

[a] Bond labels correspond to labels in Figures 1−4. (Bonds marked "n/a" correspond to failed optimizations of the dissociation intermediate.) [b] MP4(SDQ) and CCSD(T) results are derived from single energy points at MP2 optimized geometries.

TABLE 3: Bond-Breaking Energies for the Nitrogen−Nitrogen Bonds in the $N_6C_6H_6$ Isomers (Energies in kcal/mol)

method	basis set	isomer 6	isomer 0	isomer 4	isomer 2
MP2	aug-cc-pVDZ	+44.9	+46.5	+62.5	+53.1
MP4(SDQ)[a]	aug-cc-pVDZ	+33.3	+31.9	+49.2	+38.8
MP2	cc-pVTZ	+45.2	+48.8	+65.1	+56.6
MP4(SDQ)[a]	cc-pVTZ	+33.2	+33.8	+51.0	+41.6

[a] MP4(SDQ) energies calculated at MP2 geometries optimized with the same basis set.

TABLE 4: Free Energies of Detonation for Isomers of $N_6C_6H_6$[a]

reaction		kcal/mol	kcal/g
$N_6C_6H_6 \rightarrow 3N_2 + C_6H_6$	isomer 6	−271.0	−1.67
(no atmosphere)	isomer 0	−262.3	−1.62
	isomer 4	−219.4	−1.35
	isomer 2	−215.7	−1.33
$N_6C_6H_6 + (15/2)O_2 \rightarrow 3N_2 + 6CO_2 + 3H_2O$	isomer 6	−1249.4	−7.71
(oxygen atmosphere)	isomer 0	−1240.7	−7.66
	isomer 4	−1197.8	−7.39
	isomer 2	−1194.1	−7.37

[a] Energies are calculated with the B3LYP/cc-pVDZ method. Results are calculated for various assumptions regarding the atmosphere in which the detonation occurs.

stability advantage in each case lies with the molecule with fewer carbons in the axial triangles. Isomer 0 has more than a 10 kcal/mol advantage over isomer 6, and isomer 2 has a 4−5 kcal/mol advantage over isomer 4. Interestingly, although the previous problem of the instability[7] of N_{12} was solved by substitution of carbon atoms into the axial triangles,[27] such a substitution fails to maximize the number of C−N bonds and is therefore not the optimal approach to a stable $N_6C_6H_6$.

Bond-Breaking Stability. Do the advantages that lead to isomer vs isomer stability also lead to advantages in resistance to bond breaking? Table 2 shows the bond-breaking energies for the $N_6C_6H_6$ cages, calculated with the cc-pVDZ basis set. Isomer 6 and isomer 0 have D_{3d} point group symmetry and three symmetry-independent bonds each. Isomers 4 and 2 both have C_{2h} point group symmetry and six symmetry-independent bonds each. For the four molecules in this study, the B3LYP dissociation energies are consistently low and the MP2 energies are consistently much higher, with MP4 and CCSD(T) energies (presumably the most accurate in the study) lying between and agreeing well with each other. All methods in this study agree that the NN bond in each molecule has the lowest dissociation energy for that molecule. It is likely that a dissociation mechanism for any of these molecules would begin with the breaking of an NN bond. However, although the NN bond is the weakest link in all the molecules, the NN bonds display a substantial variation in the dissociation energies. Isomers 6 and 0 can break an NN bond with an energy a little over 30 kcal/mol. The NN bond of isomer 2 requires over 40 kcal/mol to break, and isomer 4 requires nearly 50 kcal/mol to break the NN bond. Table 3 shows results with larger basis sets, and the numbers generally point to slight increases in dissociation energies when larger basis sets are employed. Isomer 4 is the most stable with respect to dissociation.

The variations in the NN bond-breaking energies may be due to the bonding environment surrounding the NN bonds in each molecule. Because each nitrogen atom is three-coordinate, each NN bond is surrounded by four other bonds in the local environment. In isomers 6 and 0, the environment consists of two NN bonds and two CN bonds (which are stronger than NN bonds), and these two isomers have the lowest NN bond-breaking energies. In contrast, isomers 4 and 2 have NN bonds surrounded by four CN bonds. The environment of stronger bonds in isomers 4 and 2 may cause the NN bonds themselves to be stronger than the corresponding bonds in isomers 6 and 0. The difference between isomers 4 and 2 is probably due to the fact that the NN bonds in isomer 2 belong to ring-strained triangles. The release of ring strain by opening an NN bond in isomer 2 makes the bond-breaking energy lower than the NN bond-breaking energy of isomer 4.

Detonation Energies. Table 4 shows the detonation energies of the four molecules in this study. Isomers 4 and 2 are more stable than isomers 6 and 0 by about 0.3 kcal/g, which lowers the detonation energies of isomers 4 and 2 by the same amount. The specific reaction of detonation depends on what assumptions are made about the available atmosphere. Without an atmosphere of any kind, the detonation energy comes from the decomposition of the nitrogen to N_2. If plentiful oxygen is assumed, then additional energy will result from combustion of the hydrocarbon content. For detonation without atmosphere, isomers 4 and

2 produce about 20% less energy than isomers 6 and 0. For detonation in oxygen, the variation among isomers is less than 5%.

Conclusion

Stability of $N_6C_6H_6$ cages is determined by the arrangement of the carbon and nitrogen atoms, and maximizing the number of C−N bonds is the primary stabilizing factor. For all molecules in this study, the N−N bond is the weakest, meaning that the strength of the N−N bond should determine the molecule's resistance to dissociation. The isomers exhibit significant differences in the strength of the N−N bond, but all of the molecules have N−N dissociation energies of at least 30 kcal/mol. Therefore, any of the isomers has potential as an HEDM and increases in stability come at a cost in terms of lower detonation energies.

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Supporting Information Available: Symmetries of the dissociation intermediates. This material is available free of charge via the Internet at http://pubs.acs.org.

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