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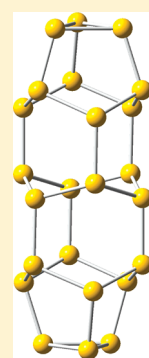
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N₂₂C₂ versus N₂₄: Role of Molecular Curvature in Determining Isomer Stability

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ABSTRACT: Three-dimensional N₂₂C₂ cages are examined by theoretical calculations to determine relative stability among various isomers. Stability as a function of cage shape and stability as a function of carbon location are calculated and discussed. The results are compared to isomers of N₂₄ to determine the effects of carbon substitution into the cage structure. Further, since the various cage shapes in this study vary by degree of curvature, model calculations are carried out to determine the energetic consequences of curving the local structure around nitrogen and carbon. The model calculations are compared to the actual results on the larger cages to determine how well curvature effects explain the relative stability of N₂₂C₂ isomer as compared to the corresponding N₂₄.



■ INTRODUCTION

Molecules consisting entirely or predominantly of nitrogen are of interest for their potential as high-energy materials. Decomposition reactions of the type $N_x \rightarrow (x/2) N_2$ are strongly exothermic. Experimental syntheses of such molecules include the pentanitrogen (N₅) cation and anion.^{1–3} Various azides^{4,5} and polyazides^{6,7} have been synthesized, as well as a network polymer⁸ of nitrogen under high-pressure conditions. Azo compounds^{9,10} with high nitrogen content have also been synthesized. A substantial body of theoretical research on cyclic and acyclic nitrogen molecules^{11–16} has been carried out, as well as investigations into the properties of nitrogen cages.^{17–23} Several of these theoretical studies, however, predict the subject molecules to be unstable with respect to dissociation.

In particular, several isomers of N₂₄ cages have been studied²⁴ theoretically, with the result that nitrogen favors a cylindrical cage structure over a more spherical one. Such cages, if synthesized, would likely have low energy paths to dissociation, but carbon atoms have been previously shown²⁵ to stabilize nitrogen cages. However, carbon cages prefer the well-known spherical structures that are exhibited by molecules such as buckminsterfullerene (C₆₀). Therefore, the introduction of carbon into otherwise all-nitrogen cages is likely to significantly change the energetic relationships between the various isomers. In this study, the three most stable N₂₄ cages are examined to determine the effects of carbon substitution into the structure. C₂ units are substituted into various sites on the cages, and theoretical calculations are carried out to answer two fundamental questions: which sites for carbon substitution lead to the most stable isomers, and how does the carbon substitution affect the relationships between isomers?

■ COMPUTATIONAL METHODS

Geometries in this study are optimized using Hartree–Fock theory and density functional theory²⁶ (PBE1PBE). Single-point

energies are calculated using coupled-cluster theory²⁷ (CCSD(T)). The Dunning cc-pVDZ basis set²⁸ is used for all calculations in this study. All calculations are carried out in the singlet electronic state. Calculations are carried out using the Gaussian03 computational chemistry software²⁹ and its Windows counterpart Gaussian03W.

■ RESULTS AND DISCUSSION

The three isomers of N₂₄ are shown in Figure 1. Isomer T is the most stable N₂₄, has triangles on each end, and has *D*_{3d} point group symmetry. Isomer S has squares on each end and *D*_{4h} symmetry. Isomer H is a hexagonal isomer with *D*_{6d} symmetry. Previous calculations²⁴ on N₂₄ have shown that the T isomer is the most stable, by about 70 kcal/mol with respect to the S isomer and by about 100 kcal/mol with respect to the H isomer. The N₂₂C₂ isomers in this study are generated by substituting C₂ units into the various N₂₄ frameworks; in all cases, the two carbons are bonded to each other by a formal double bond. The T framework has five symmetry-independent substitution sites, the S framework has four, and the H framework has three. Therefore, 12 isomers of N₂₂C₂ are under consideration in this study. The substitution sites for all 12 isomers are shown in Figure 2.

Geometries and energies for all 12 N₂₂C₂ isomers have been calculated, and the results are shown in Table 1. The results reflect the differences between an sp³ hybridized N₂ unit, which prefers pyramidal environments and tetrahedral bond angles, and an sp² hybridized C₂, which prefers planar environments and 120° bond angles. The inclusion of the C₂ unit introduces

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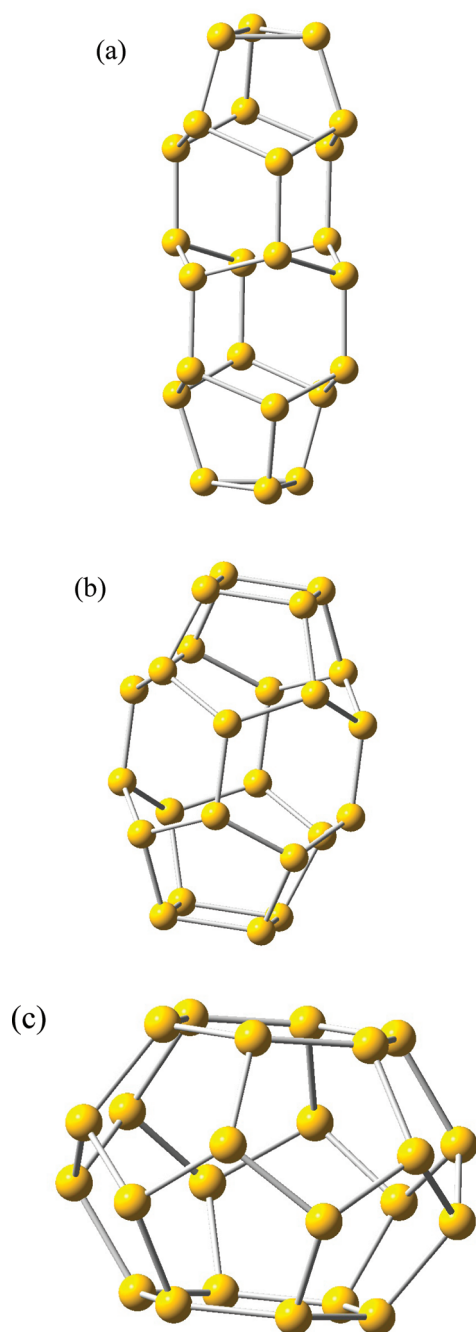


Figure 1. N_{24} isomers. (a) T isomer; (b) S isomer; (c) H isomer.

$\pi-\pi^*$ molecular orbitals that resist torsion and curvature. Isomers T1, T2, S1, and S2 are heavily penalized by having carbon atoms in a tight polygon, either a triangle or square. On all three frameworks, the most stable isomer is the one that places the C_2 unit in the most planar environment with the least angular and torsional strain. Isomers T4, S4, and H1 are the most stable isomers on their respective frames. All three theoretical methods agree on the energy ordering of the various isomers, although coupled-cluster theory varies the energy differences somewhat. Some of the PBE1PBE geometry optimizations were dissociative, as were some of the B3LYP optimizations²⁴ in the previous N_{24} study. Nevertheless, PBE1PBE successfully optimizes the most stable isomer on each frame, and the three methods are in good agreement.

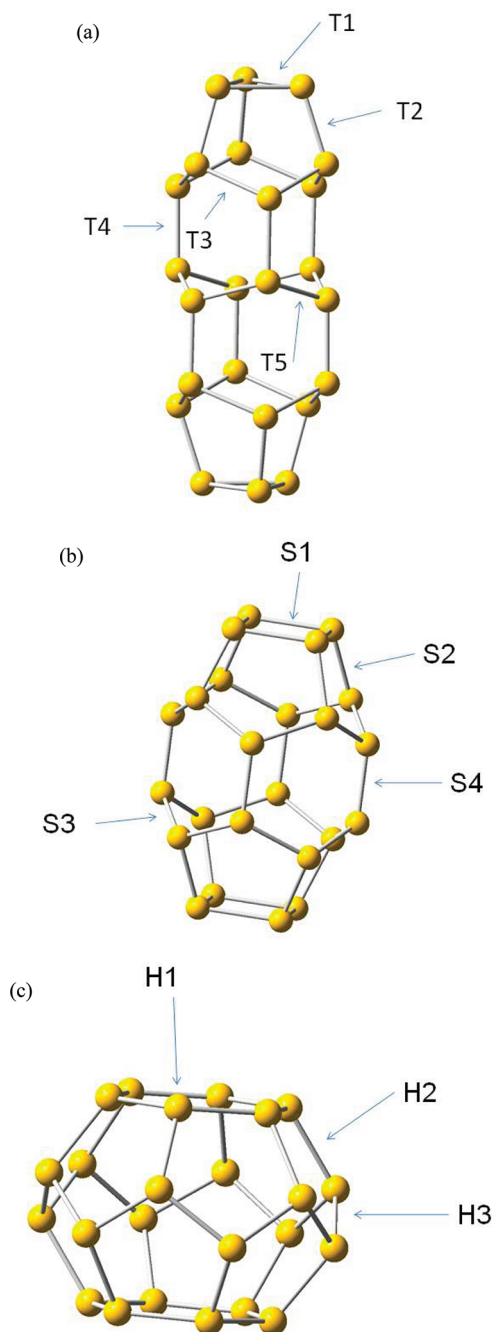


Figure 2. $N_{22}C_2$ isomers, with labels indicating the symmetry-independent C_2 substitution sites. (a) Substitution sites for five $N_{22}C_2$ isomers based on the T framework. (b) Substitution sites for four $N_{22}C_2$ isomers based on the S framework. (c) Substitution sites for three $N_{22}C_2$ isomers based on the H framework.

Table 2 compares the most stable isomers of $N_{22}C_2$ with the corresponding structures from the previous study²⁴ of N_{24} . The N_{24} isomers have been reoptimized with the PBE1PBE/cc-pVDZ method since B3LYP was the density functional method of choice in the original N_{24} study. The triangular isomer is the most stable in all cases, but when the C_2 is introduced to form $N_{22}C_2$, the S and H isomers are substantially lowered in energy relative to the T isomer. Relative to the T isomer, the S and H isomers are favored by about 40 kcal/mol with HF/cc-pVDZ and by 27–28 kcal/mol with PBE1PBE/cc-pVDZ.

Table 1. Relative Energies of $N_{22}C_2$ Isomers (Energies in kcal/mol)^a

	HF	PBE1PBE	CCSD(T)/HF
T1	+82.0	+86.7	+82.5
T2	+70.9	+69.2	+67.5
T3	+34.9	^b	+30.2
T4	0.0	0.0	0.0
T5	+21.7	^b	+11.1
S1	+115.2	+111.7	+117.3
S2	+88.1	+79.1	+90.8
S3	+54.5	^b	+59.9
S4	+36.6	+40.7	+44.9
H1	+62.2	+69.3	+73.5
H2	+77.9	+78.5	+84.0
H3	+102.8	^b	+104.8

^a All calculations are carried out using the cc-pVDZ basis set. ^b Several of the PBE1PBE geometry optimizations were dissociative.

Table 2. Comparison of Isomer Energy Relationships between N_{24} and $N_{22}C_2$ ^a

isomer	HF/cc-pVDZ		PBE1PBE/cc-pVDZ	
	N_{24}	$N_{22}C_2$	N_{24}	$N_{22}C_2$
T/T4	0.0	0.0	0.0	0.0
S/S4	+73.7	+36.6	+67.6	+40.7
H/H1	+104.1	+62.2	+97.9	+69.3

^a Labels T, S, and H refers to structures of N_{24} . Labels T4, S4, and H1 refer to the most stable $N_{22}C_2$ on each framework. Energies in kcal/mol.

The primary difference between the T, S, and H frameworks is the degree of curvature in the structure, with the highly cylindrical T framework being the most tightly curved. The tight curvature of the T structure would be expected to be the most favorable to pyramidal nitrogen and least favorable to planar carbon. Therefore, substitution of carbon for nitrogen on the T framework would be expected to be energetically penalized. Can this effect be quantified to test this idea? Regarding the local structure around carbon on the T4, S4, and H1 isomers, the dihedral angles around the C_2 unit are approximately 130° for the T4 isomer and approximately 150° for S4 and H1. These curvatures can be modeled by the model system shown in Figure 3. The structure shown in Figure 3 can be reoptimized with a constrained dihedral angle around the central atoms, and the results can be compared to approximate the effects of geometric curvature. The results of these calculations for carbon curvature and nitrogen curvature are shown in Table 3.

The difference between N_{24} and $N_{22}C_2$ derives from two curvature effects: (1) the loss of the nitrogen advantage for the more tightly curved T isomer, and (2) the addition of the carbon penalty for the more tightly curved T isomer. When N_2 is replaced by C_2 in the N_{24} framework, the change in isomer energies is affected by both curvature effects, which can be considered to be roughly additive. The data in Table 3 suggest that the substitution of C_2 to form the T4 isomer of $N_{22}C_2$ should lower the energy of S4 and H1 relative to T4. The relative energies between the framework isomers should change by 37.5 kcal/mol for HF/cc-pVDZ and 32.7 kcal/mol for PBE1PBE/cc-pVDZ, figures that agree reasonably well with the actual isomer energy changes shown in Table 2.

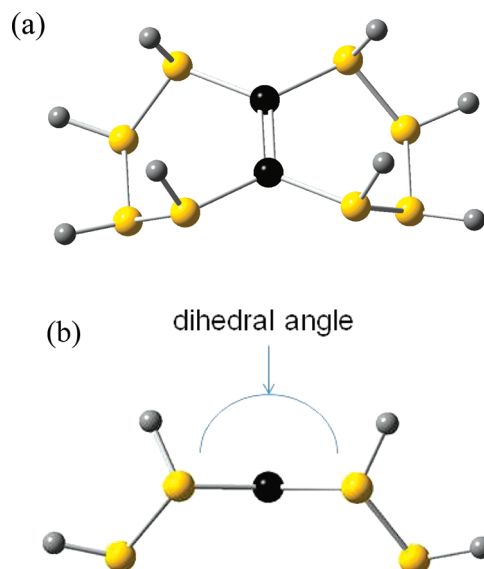


Figure 3. Two views of the model system for calculating curvature effects in nitrogen networks and carbon–nitrogen networks. The system is shown for carbon (atoms in black), with nitrogen in yellow and hydrogen in gray. When curvature effects for nitrogen are calculated, the two center atoms are also nitrogen. (a) Illustrative view showing all atoms. (b) Edge view showing the dihedral angle used to model curvature.

Table 3. Curvature Effects for a C_2 Unit in a Nitrogen Network versus a N_2 Unit in the Same Network^a

curvature angle	HF/cc-pVDZ		PBE1PBE/cc-pVDZ	
	carbon	nitrogen	carbon	nitrogen
130° (as in T isomer)	0.0	0.0	0.0	0.0
150° (as in S or H isomer)	−23.2	+14.3	−18.0	+14.7

^a Relative energies in kcal/mol.

The energy differences between the $N_{22}C_2$ isomers are well explained by curvature effects for carbon and nitrogen.

CONCLUSION

The preference of nitrogen for cylindrical networks and the preference of carbon for spheroidal networks is the result of differences in the way the two elements are affected by structural curvature. Those energetic effects have now been quantified for a small model system whose results agree well with the energies of the larger cage molecules. N_{24} favors a cylinder, whereas C_{24} favors a spheroid. $N_{22}C_2$ shows the effects of incremental replacement of nitrogen with carbon. The incremental substitution of carbon into the nitrogen network should lead to a crossover structure for which the various shapes become approximately isoenergetic. Additionally, the incremental addition of carbon may lead to stable structures that can be synthesized and used in high-energy applications.

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