Research Article

Carbon Substitution on N$_{24}$ Cages: Crossover between Triangular and Hexagonal Structures

Carrie Sanders and Douglas L. Strout

Department of Physical Sciences, Alabama State University, Montgomery, AL 36101, USA

Correspondence should be addressed to Douglas L. Strout; dstrout@alasu.edu

Received 25 May 2013; Revised 29 July 2013; Accepted 1 August 2013

Academic Editor: Abdou Boucekkine

Copyright © 2013 C. Sanders and D. L. Strout. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Complex forms of nitrogen are of interest for their potential as high-energy materials, but many all-nitrogen systems lack the stability for practical high-energy applications. Inclusion of carbon atoms in an otherwise all-nitrogen structure can increase stability. Nitrogen cages are known for energetically preferring cylindrical structures with triangular endcaps, but carbon cages prefer the pentagon-hexagon structure of the fullerenes. Previous calculations on N$_{22}$C$_2$ have shown that carbon inclusion narrows the gap between triangular and fullerene-like structures. In the current study, three isomers of N$_{24}$ are used as frameworks for carbon substitution. Theoretical calculations are carried out on isomers of N$_{20}$C$_4$, N$_{18}$C$_6$, and N$_{16}$C$_8$, with the goal of determining what level of carbon substitution causes the carbon fullerene-like structures to become energetically preferred.

1. Introduction

Complex nitrogen molecules are of interest for their potential as high-energy materials. Synthetic successes [1–4] such as the N$_5^+$ and N$_5^-$ ions, as well as various azido compounds [5–10] and even a network polymer of nitrogen [11], demonstrate the potential for novel high-energy molecules. Theoretical studies of high-energy nitrogen include cyclic and acyclic compounds [12–19], as well as nitrogen cages [20–26]. A theoretical study [27] of N$_{24}$ cages predicted that N$_{24}$ prefers a tightly curved, cylindrical structure with triangular endcaps. Many all-nitrogen molecules dissociate with low barriers, which limits the utility of these molecules in energetic applications. Incorporation of heteroatoms such as carbon into an otherwise all-nitrogen molecule can increase stability, but the resulting molecule would still be highly energetic. If carbon atoms are incorporated into a nitrogen cage structure, would the structure still energetically prefer a cylindrical structure?

The behavior of nitrogen stands in contrast to the well-known behavior of carbon, whose most stable cages are spheroidal in shape and consist of pentagons and hexagons. A previous study [28] on N$_{22}$C$_2$ cages illustrated this difference between carbon and nitrogen. The triangular, cylindrical form of N$_{22}$C$_2$ is the most stable isomer, but the energy difference between the cylinder and the spheroid is less than that for the same isomers of N$_{24}$. Carbon substitution stabilizes the spheroidal isomer relative to the others. Since C$_{24}$ prefers a spheroidal structure, additional incremental substitution of additional carbon on N$_{24}$ must necessarily lead to an energetic crossover from favoring the cylinder to favoring the spheroid. In the current study, the N$_{22}$C$_2$ results are extended by theoretical calculations to N$_{20}$C$_4$, N$_{18}$C$_6$, and N$_{16}$C$_8$, and so forth, to determine the cage composition at which the structural crossover occurs. Triangular, square, and hexagonal isomers from the N$_{24}$ study are used as the basis for carbon substitution.

2. Computational Methods

Geometries are optimized with the Hartree-Fock method. Single-energy points are calculated with the PBE1PBE density functional method [29–31] and with coupled-cluster theory [32, 33] (CCSD(T)). Hartree-Fock is used for geometries for the following two reasons. (1) The previous study on N$_{24}$ showed that the isomer energies do not depend strongly on the choice of geometry. (2) Some of the PBE1PBE geometry...
optimizations are dissociative. However, PBE+PBE optimizations have been carried out successfully for \( \text{N}_{16}\text{C}_8 \). All molecules in this study have been confirmed as local minima by Hartree-Fock vibrational frequencies. All calculations in this study are carried out with the Dunning cc-pVDZ atomic orbital basis set [34]. The Gaussian09 computational chemistry software [35], along with its Windows counterpart Gaussian09W, is used for all calculations in this study.

3. Results and Discussion

The three \( \text{N}_{24} \) frameworks in this study are shown in Figure 1. They include the triangular (T) cylinder, the hexagonal (H) fullerene-like spheroid, and a square (S) isomer with fourfold symmetry. Carbon atoms are substituted on these structures in \( \text{C}_2 \) pairs sharing a C=C double bond, whose strong bond enthalpy should lend stability to the molecule. Additionally, structures with isolated carbon atoms necessarily have either strong formal charges or open-shell electrons. Carbon substitution isomers are selected for study based on criteria established by the \( \text{N}_{22}\text{C}_2 \) study. The T isomer energetically prefers carbon substitution parallel to the long axis of the molecule. The H isomer prefers carbon substitution in the hexagons themselves, and the S isomer prefers substitution at the molecule’s equator, parallel to the \( \text{C}_4 \) axis. Additionally, the \( \text{C}_2 \) pairs are isolated from each other, because increasing
Figure 3: Isomers of N$_{18}$C$_6$: (a) isomer T, (b) isomer S, (c) isomer H1, and (d) isomer H2. Carbon atoms are shown in black, and nitrogen atoms are shown in yellow.

Figure 4: Isomers of N$_{16}$C$_8$: (a) isomer S, (b) isomer H1, and (c) isomer H2. Carbon atoms are shown in black, and nitrogen atoms are shown in yellow.
The number of C–C bonds also increases the number of N–N bonds, which have very low bond enthalpy.

$N_{20}C_4$. The above criteria generate eight isomers of $N_{20}C_4$, which are shown in Figure 2. Relative energies of the eight molecules are tabulated in Table 1. Several trends appear in the data. For each structural framework, the lowest energy isomer is one in which the two C2 pairs are far apart. This may be due to the polarization of the C–N bonds around the C2 pairs; each bond would polarize the nitrogen negatively, and negatively charged nitrogens in close proximity to each other would be energetically unfavorable. Also, the lowest energy hexagonal isomer H4 is only (with CCSD(T) theory) about 40 kcal/mol higher in energy than T1, compared with an energy gap of about 70 kcal/mol for $N_{22}C_3$ and 100 kcal/mol for $N_{24}$. The progressive favoring of the hexagonal isomer with increasing carbon is evident. Additionally, square isomer S2 is less than 20 kcal/mol above T1.

$N_{18}C_6$. Four isomers of $N_{18}C_6$ are shown in Figure 3, and their energies are shown in Table 2. The only T isomer meeting the previous criteria of carbon substitution parallel to the C3 axis while also avoiding C2 chains has three C2 pairs on the same end of the molecule. As the number of carbon atom pairs increases, the options for a stable triangular cage decrease rapidly. The S and H isomers of $N_{18}C_6$ are much more stable than the T isomer. With three carbon pairs, the triangular isomer is no longer the most stable, and any additional carbon would further penalize the triangular framework energetically. Interestingly, the S isomer is the most stable for $N_{18}C_6$, but additional carbon substitution is still expected to favor the hexagonal isomer, which in the limit of 100% carbon would be the well-known C24 fullerene.

$N_{16}C_8$. The above criteria generate four isomers of $N_{16}C_8$, which are shown in Figure 4. The only T isomer meeting the previous criteria of carbon substitution parallel to the C3 axis while also avoiding C2 chains has three C2 pairs on the same end of the molecule. As the number of carbon atom pairs increases, the options for a stable triangular cage decrease rapidly. The S and H isomers of $N_{16}C_8$ are much more stable than the T isomer. With three carbon pairs, the triangular isomer is no longer the most stable, and any additional carbon would further penalize the triangular framework energetically. Interestingly, the S isomer is the most stable for $N_{16}C_8$, but additional carbon substitution is still expected to favor the hexagonal isomer, which in the limit of 100% carbon would be the well-known C24 fullerene.
on would only increase the hexagonal structure’s energetic advantage.

**Heat of Formation.** The energetic properties of the molecules in this study are shown in Table 4 as heat of formation calculated using CCSD(T)/HF energies. Heat of formation is calculated using the following isodesmic equations:

\[ \text{N}_2\text{C}_4 + 48\text{NH}_3 \rightarrow 2\text{C}_2\text{H}_4 + 34\text{N}_2\text{H}_4 \]
\[ \text{N}_2\text{C}_6 + 48\text{NH}_3 \rightarrow 3\text{C}_2\text{H}_4 + 33\text{N}_2\text{H}_4 \]
\[ \text{N}_2\text{C}_8 + 48\text{NH}_3 \rightarrow 4\text{C}_2\text{H}_4 + 32\text{N}_2\text{H}_4 \]

Heat of formation for \( \text{NH}_3, \text{C}_2\text{H}_4, \) and \( \text{N}_2\text{H}_4 \) is taken from the Computational Chemistry Comparison and Benchmark Database, [http://cccbdb.nist.gov/](http://cccbdb.nist.gov/). Since the energy release from the molecules derives from the decomposition of the nitrogen, the heat of formation of these molecules would be expected to decrease with increasing the carbon content. The energetic trend is shown in Table 4, but even with eight-carbon atoms, the molecules have a very high heat of formation. Any of the molecules in this study would be a high-energy material that releases large amounts of energy on decomposition.

### 4. Conclusion

Following previous trends established for \( \text{N}_2\text{C}_4 \) and \( \text{N}_2\text{C}_2 \), carbon substitution on nitrogen cages progressively favors the fullerene-like structures favored by all-carbon systems. With eight-carbon atoms, the hexagonal isomer crosses over all other isomers and becomes the energetically preferred form. Even with a composition of two-thirds of nitrogen and one-third of carbon, the \( \text{N}_2\text{C}_8 \) hexagonal isomer should be highly energetic and, if synthesized, have potential as a high-energy material.

### Acknowledgments

The Alabama Supercomputer Authority is gratefully acknowledged for a grant of computer time on the SGI Altix in Huntsville, AL, USA. This work was supported by the National Science Foundation (NSF/HBCU-UP Grant 0505872). Carrie Sanders is supported by NSF/HBCU-UP as an undergraduate STEM Scholar. This work was also supported by the National Institutes of Health (NIH/NCMHD 1P20MD00547-01) and the Petroleum Research Fund, administered by the American Chemical Society (PRF 43798-B6). The taxpayers of the state of Alabama in particular and the United States in general are gratefully acknowledged.

### References


