

## 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](mailto: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 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

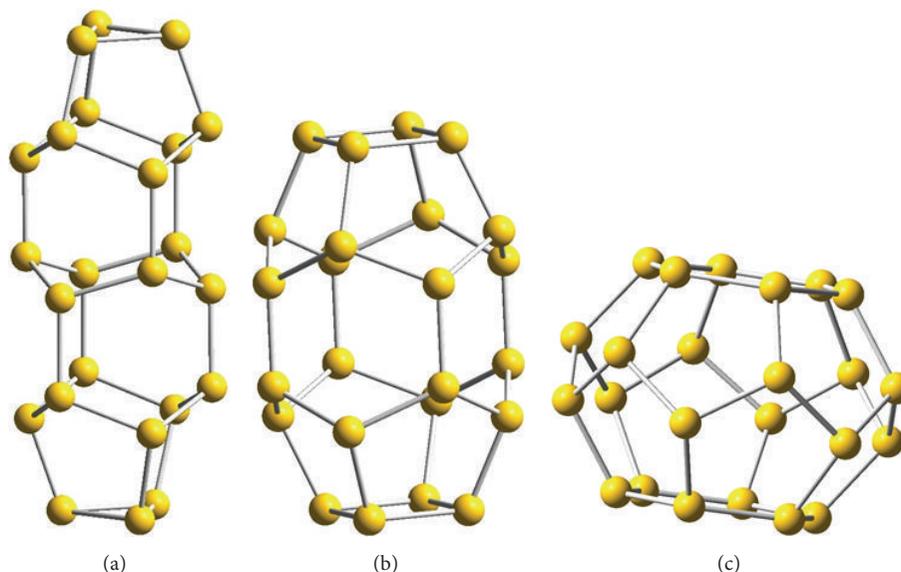


FIGURE 1: Isomers of  $N_{24}$ : (a) triangular (T) isomer, (b) square (S) isomer, and (c) hexagonal (H) isomer.

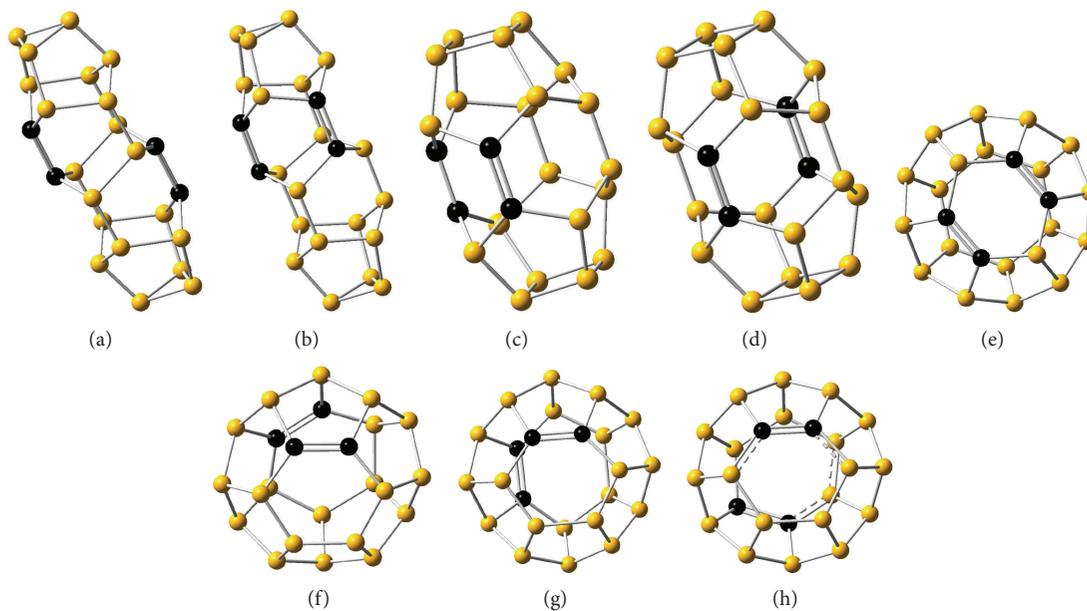


FIGURE 2: Isomers of  $N_{20}C_4$ : (a) isomer T1, (b) isomer T2, (c) isomer S1, (d) isomer S2, (e) isomer H1, (f) isomer H2, (g) isomer H3, and (h) isomer H4. Carbon atoms are shown in black, and nitrogen atoms are shown in yellow.

optimizations are dissociative. However, PBE1PBE optimizations have been carried out successfully for  $N_{16}C_8$ . 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  $N_{24}$  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  $C_2$  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  $N_{22}C_2$  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  $C_4$  axis. Additionally, the  $C_2$  pairs are isolated from each other, because increasing

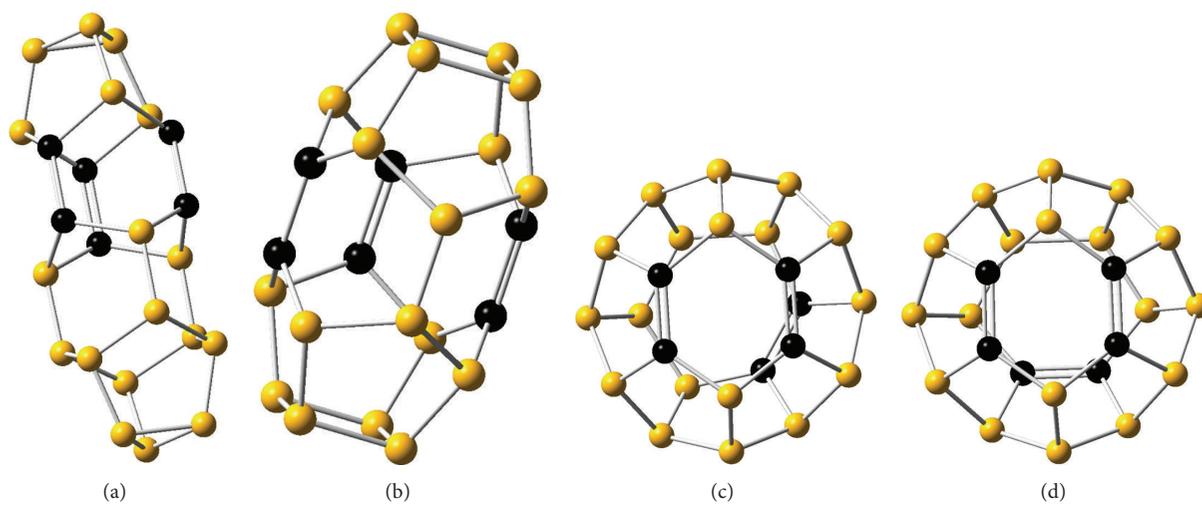


FIGURE 3: Isomers of  $N_{18}C_6$ : (a) isomer T, (b) isomer S, (c) isomer H1, and (d) isomer H2. Carbon atoms are shown in black, and nitrogen atoms are shown in yellow.

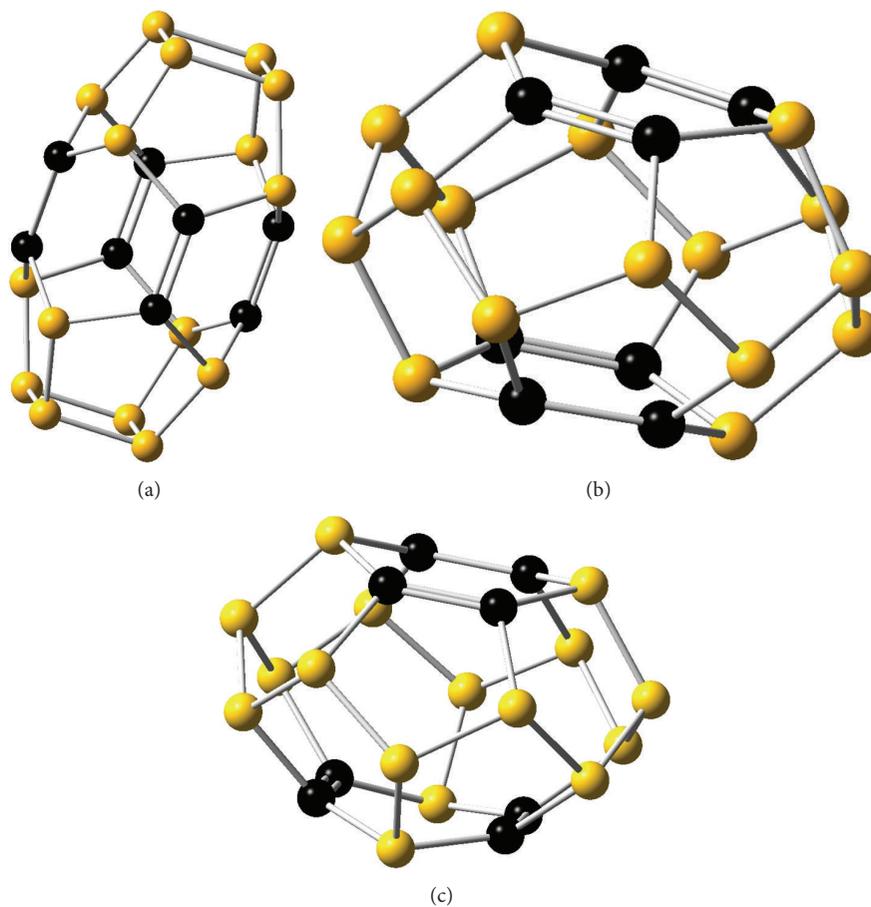


FIGURE 4: Isomers of  $N_{16}C_8$ : (a) isomer S, (b) isomer H1, and (c) isomer H2. Carbon atoms are shown in black, and nitrogen atoms are shown in yellow.

TABLE 1: Relative energies of  $N_{20}C_4$  isomers are shown in Figure 2. All energies are calculated with cc-pVDZ basis set. Energies are in kcal/mol. Point group symmetries of each isomer are listed with the isomer name.

Molecule	HF	PBE1PBE//HF	CCSD(T)//HF
T1 ( $C_{2h}$ )	0.0	0.0	0.0
T2 ( $C_s$ )	+7.3	+4.8	+6.7
S1 ( $C_{2v}$ )	+9.0	+20.5	+26.5
S2 ( $D_{2h}$ )	+1.9	+13.9	+16.5
H1 ( $C_{2v}$ )	+31.0	+49.9	+55.2
H2 ( $C_2$ )	+21.4	+40.1	+44.0
H3 ( $C_2$ )	+21.2	+39.0	+42.6
H4 ( $C_2$ )	+20.1	+37.0	+40.9

TABLE 2: Relative energies of  $N_{18}C_6$  isomers are shown in Figure 3. All energies are calculated with cc-pVDZ basis set. Energies are in kcal/mol. Point group symmetries of each isomer are listed with the isomer name.

Molecule	HF	PBE1PBE//HF	CCSD(T)//HF
T ( $C_{3v}$ )	0.0	0.0	0.0
S ( $C_{2v}$ )	-55.0	-46.7	-39.5
H1 ( $C_1$ )	-48.0	-32.9	-26.0
H2 ( $C_s$ )	-46.9	-31.3	-24.7

TABLE 3: Relative energies of  $N_{16}C_8$  isomers are shown in Figure 4. All energies are calculated with cc-pVDZ basis set. Energies are in kcal/mol. Point group symmetries of each isomer are listed with the isomer name.

Molecule	S ( $D_{4h}$ )	H1 ( $D_2$ )	H2 ( $D_{2d}$ )
HF	0.0	-6.9	-4.2
PBE1PBE//HF	0.0	-4.6	+0.4
PBE1PBE	0.0	-6.0	-1.3
CCSD(T)//HF	0.0	-4.8	-0.8
CCSD(T)//PBE1PBE	0.0	-7.6	-4.1

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  $C_2$  pairs are far apart. This may be due to the polarization of the C-N bonds around the  $C_2$  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  $N_{22}C_2$  and 100 kcal/mol for  $N_{24}$ . The progressive favoring of the hexagonal isomer

TABLE 4: Heat of formation for  $N_{20}C_4$ ,  $N_{18}C_6$ , and  $N_{16}C_8$ . Energies are calculated using CCSD(T)//HF energies. Energies are in kcal/mol and kcal/g.

Molecule	Isomer	$\Delta H_f$ (kcal/mol)	$\Delta H_f$ (kcal/g)
$N_{20}C_4$ ( $M = 328$ g/mol)	T1	+1003.8	+3.06
	T2	+1010.5	+3.08
	S1	+1030.3	+3.14
	S2	+1020.3	+3.11
	H1	+1059.0	+3.23
	H2	+1047.8	+3.19
	H3	+1046.4	+3.19
	H4	+1044.7	+3.19
$N_{18}C_6$ ( $M = 324$ g/mol)	T	+988.0	+3.05
	S	+948.5	+2.93
	H1	+962.0	+2.97
$N_{16}C_8$ ( $M = 320$ g/mol)	H2	+963.3	+2.97
	S	+880.1	+2.75
	H1	+875.5	+2.74
	H2	+879.3	+2.75

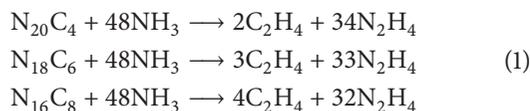
with increasing carbon is evident. Additionally, square isomer S2 is less than 20 kcal/mol above T1.

$N_{18}C_6$ . 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  $C_3$  axis while also avoiding  $C_4$  chains has three  $C_2$  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  $C_{24}$  fullerene.

$N_{16}C_8$ . Since the T isomer of  $N_{18}C_6$  is so much less stable than the others, only S and H energies are shown in Table 3. Isomer H1 is the most stable, and therefore  $N_{16}C_8$  is the crossover composition for the 24-atom hexagonal framework. The theory methods in this study disagree as to whether isomer H2 is more stable than S for  $N_{16}C_8$ , but the stability of H1 is sufficient to demonstrate the crossover to favoring hexagonal structure. Table 3 also shows that geometry effects are small. PBE1PBE optimizations on all three  $N_{16}C_8$  isomers have been carried out, and all theory methods agree within a few kcal/mol regardless of the choice of optimization method. Isomer H1 is the most stable with all theory methods. Any further carbon substitution to  $N_{14}C_{10}$ ,  $N_{12}C_{12}$ , and so

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:



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/>. 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  $\text{N}_{24}$  and  $\text{N}_{22}\text{C}_2$ , 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  $\text{N}_{16}\text{C}_8$  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 IP20MD000547-01) 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

- [1] K. O. Christe, W. W. Wilson, J. A. Sheehy, and J. A. Boatz, " $\text{N}_5^+$ : a novel homoleptic polynitrogen ion as a high energy density material," *Angewandte Chemie—International Edition*, vol. 38, no. 13-14, pp. 2004–2009, 1999.
- [2] A. Vij, J. G. Pavlovich, W. W. Wilson, V. Vij, and K. O. Christe, "Experimental detection of the pentaazacyclopentadienide (pentazolite) anion, *cyclo-N}\_5^+*," *Angewandte Chemie—International Edition*, vol. 41, no. 16, pp. 3051–3054, 2002.
- [3] R. N. Butler, J. C. Stephens, and L. A. Burke, "First generation of pentazole ( $\text{HN}_5$ , pentazolic acid), the final azole, and a zinc pentazolite salt in solution: a new N-dearylation of 1-(p-methoxyphenyl) pyrazoles, a 2-(p-methoxyphenyl) tetrazole and application of the methodology to 1-(p-methoxyphenyl) pentazole," *Chemical Communications*, vol. 8, pp. 1016–1017, 2003.
- [4] D. A. Dixon, D. Feller, K. O. Christe et al., "Enthalpies of formation of gas-phase  $\text{N}_3$ ,  $\text{N}_3^-$ ,  $\text{N}_5^+$ , and  $\text{N}_5^-$  from Ab initio molecular orbital theory, stability Predictions for  $\text{N}_5^+\text{N}_3^-$  and  $\text{N}_5^+\text{N}_5^-$ , and experimental evidence for the instability of  $\text{N}_5^+\text{N}_3^-$ ," *Journal of the American Chemical Society*, vol. 126, no. 3, pp. 834–843, 2004.
- [5] C. Knapp and J. Passmore, "On the way to "solid nitrogen" at normal temperature and pressure? Binary azides of heavier group 15 and 16 elements," *Angewandte Chemie—International Edition*, vol. 43, no. 37, pp. 4834–4836, 2004.
- [6] R. Haiges, S. Schneider, T. Schroer, and K. O. Christe, "High-energy-density materials: synthesis and characterization of  $\text{N}_5^+[\text{P}(\text{N}_3)_6]^-$ ,  $\text{N}_5^+[\text{B}(\text{N}_3)_4]^-$ ,  $\text{N}_5^+[\text{HF}_2]^- \cdot n\text{HF}$ ,  $\text{N}_5^+[\text{BF}_4]^-$ ,  $\text{N}_5^+[\text{PF}_6]^-$ , and  $\text{N}_5^+[\text{SO}_3\text{F}]^-$ ," *Angewandte Chemie—International Edition*, vol. 43, no. 37, pp. 4919–4924, 2004.
- [7] M.-H. V. Huynh, M. A. Hiskey, E. L. Hartline, D. P. Montoya, and R. Gilardi, "Polyazido high-nitrogen compounds: hydrazo- and azo-1,3,5-triazine," *Angewandte Chemie—International Edition*, vol. 43, no. 37, pp. 4924–4928, 2004.
- [8] T. M. Klapotke, A. Schulz, and J. McNamara, "Preparation, characterization and ab initio computation of the first binary antimony azide,  $\text{Sb}(\text{N}_3)_3$ ," *Journal of the Chemical Society, Dalton Transactions*, no. 14, pp. 2985–2987, 1996.
- [9] T. M. Klapotke, H. Noth, T. Schutt, and M. Warchhold, "Tetraphenylphosphonium hexaazidoarsenate(V): the first structurally characterized binary  $\text{As}^{\text{V}}$ -azide species," *Angewandte Chemie—International Edition*, vol. 39, no. 12, pp. 2108–2109, 2000.
- [10] T. M. Klapotke, R. Krumm, P. Mayer, and I. Schwab, "Binary tellurium(IV) azides:  $\text{Te}(\text{N}_3)_4$  and  $[\text{Te}(\text{N}_3)_5]^-$ ," *Angewandte Chemie—International Edition*, vol. 42, no. 47, pp. 5843–5846, 2003.
- [11] M. I. Eremets, A. G. Gavriliuk, I. A. Trojan, D. A. Dzivenko, and R. Boehler, "Single-bonded cubic form of nitrogen," *Nature Materials*, vol. 3, no. 8, pp. 558–563, 2004.
- [12] G. Chung, M. W. Schmidt, and M. S. Gordon, "An Ab initio study of potential energy surfaces for  $\text{N}_3$  isomers," *The Journal of Physical Chemistry A*, vol. 104, no. 23, pp. 5647–5650, 2000.
- [13] D. L. Strout, "Acyclic  $\text{N}_{10}$  fails as a high energy density material," *Journal of Physical Chemistry A*, vol. 106, no. 5, pp. 816–818, 2002.
- [14] M. D. Thompson, T. M. Bledson, and D. L. Strout, "Dissociation barriers for odd-numbered acyclic nitrogen molecules  $\text{N}_9$  and  $\text{N}_{11}$ ," *Journal of Physical Chemistry A*, vol. 106, no. 29, pp. 6880–6882, 2002.
- [15] Q. S. Li and Y. D. Liu, "Structures and stability of  $\text{N}_{11}$  cluster," *Chemical Physics Letters*, vol. 353, no. 3-4, pp. 204–212, 2002.
- [16] Q. S. Li, H. Qu, and H. S. Zhu, "Quantum chemistry calculations of nitrogen cages  $\text{N}_{10}$ ," *Chinese Science Bulletin*, vol. 41, no. 14, pp. 1184–1188, 1996.
- [17] Q. S. Li and J. F. Zhao, "Theoretical study of potential energy surfaces for  $\text{N}_{12}$  clusters," *The Journal of Physical Chemistry A*, vol. 106, no. 21, pp. 5367–5372, 2002.
- [18] H. Qu, Q. S. Li, and H. S. Zhu, "Quantum chemical calculations of nitrogen cages  $\text{N}_{12}$ ," *Chinese Science Bulletin*, vol. 42, no. 6, pp. 462–465, 1997.

- [19] L. Gagliardi, S. Evangelisti, A. Bernhardsson, R. Lindh, and B. O. Roos, "Dissociation reaction of  $N_8$  azapentalene to  $4N_2$ : a theoretical study," *International Journal of Quantum Chemistry*, vol. 77, no. 1, pp. 311–315, 2000.
- [20] L. Gagliardi, S. Evangelisti, P. O. Widmark, and B. O. Roos, "A theoretical study of the  $N_8$  cubane to  $N_8$  pentalene isomerization reaction," *Theoretical Chemistry Accounts*, vol. 97, no. 1–4, pp. 136–142, 1997.
- [21] M. W. Schmidt, M. S. Gordon, and J. A. Boatz, "Cubic fuels?" *International Journal of Quantum Chemistry*, vol. 76, no. 3, pp. 434–446, 2000.
- [22] H. Zhou, N.-B. Wong, G. Zhou, and A. Tian, "Theoretical study on "multilayer" nitrogen cages," *Journal of Physical Chemistry A*, vol. 110, no. 10, pp. 3845–3852, 2006.
- [23] H. Zhou, N.-B. Wong, G. Zhou, and A. Tian, "What makes the cylinder-shaped  $N_{72}$  cage stable?" *Journal of Physical Chemistry A*, vol. 110, no. 23, pp. 7441–7446, 2006.
- [24] L. Y. Bruney, T. M. Bledson, and D. L. Strout, "What makes an  $N_{12}$  cage stable?" *Inorganic Chemistry*, vol. 42, no. 24, pp. 8117–8120, 2003.
- [25] S. E. Sturdivant, F. A. Nelson, and D. L. Strout, "Trends in stability for  $N_{18}$  cages," *Journal of Physical Chemistry A*, vol. 108, no. 34, pp. 7087–7090, 2004.
- [26] D. L. Strout, "Cage isomers of  $N_{14}$  and  $N_{16}$ : nitrogen molecules that are not a multiple of six," *Journal of Physical Chemistry A*, vol. 108, no. 49, pp. 10911–10916, 2004.
- [27] D. L. Strout, "Isomer stability of  $N_{24}$ ,  $N_{30}$ , and  $N_{36}$  cages: cylindrical versus spherical structure," *The Journal of Physical Chemistry A*, vol. 108, no. 13, pp. 2555–2558, 2004.
- [28] S. Jasper, A. Hammond, J. Thomas, L. Kidd, and D. L. Strout, " $N_{22}C_2$  versus  $N_{24}$ : role of molecular curvature in determining isomer stability," *Journal of Physical Chemistry A*, vol. 115, no. 42, pp. 11915–11918, 2011.
- [29] J. P. Perdew and M. Ernzerhof, "Rationale for mixing exact exchange with density functional approximations," *Journal of Chemical Physics*, vol. 105, no. 22, p. 9982, 1996.
- [30] M. Ernzerhof and G. E. Scuseria, "Assessment of the Perdew-Burke-Ernzerhof exchange-correlation functional," *Journal of Chemical Physics*, vol. 110, no. 11, p. 5029, 1999.
- [31] C. Adamo and V. Barone, "Toward reliable density functional methods without adjustable parameters: the PBE0 model," *Journal of Chemical Physics*, vol. 110, no. 13, p. 6158, 1999.
- [32] G. D. Purvis and R. J. Bartlett, "A full coupled-cluster singles and doubles model: the inclusion of disconnected triples," *Journal of Chemical Physics*, vol. 76, no. 4, p. 1910, 1982.
- [33] G. E. Scuseria, C. L. Janssen, and H. F. Schaefer III, "An efficient reformulation of the closed-shell coupled cluster single and double excitation (CCSD) equations," *Journal of Chemical Physics*, vol. 89, no. 12, p. 7382, 1988.
- [34] T. H. Dunning Jr., "Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen," *Journal of Chemical Physics*, vol. 90, no. 2, p. 1007, 1989.
- [35] M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., *Gaussian 09, Revision C.01*, Gaussian, Inc., Wallingford, Conn, USA, 2010.



**Hindawi**

Submit your manuscripts at  
<http://www.hindawi.com>

