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# Structure and Decomposition Energies of High-Energy Open-Chain Carbon–Nitrogen Compounds $N_xC_2$

Jessica Thomas, Kiara Fairman, and Douglas L. Strout\*

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

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Molecules and ions consisting entirely or predominantly of nitrogen are of interest because of their energy release properties. Such molecules can decompose into  $N_2$ , a process that is very exothermic. Following a study predicting the stability properties of isomers of open-chain  $N_4C_2$ , the current study involves calculations on a series of open-chain carbon–nitrogen molecules. Molecules with the general formulas  $N_xC_2$  are studied to determine their structure and bonding, as well as their energy release capabilities. Theoretical calculations are carried out on this series of molecules to determine geometries and heats of formation. The MP2 method is used for geometry optimizations and vibrational frequencies, with single energies calculated with coupled-cluster theory (CCSD(T)). Energetic and structural trends are calculated and discussed.

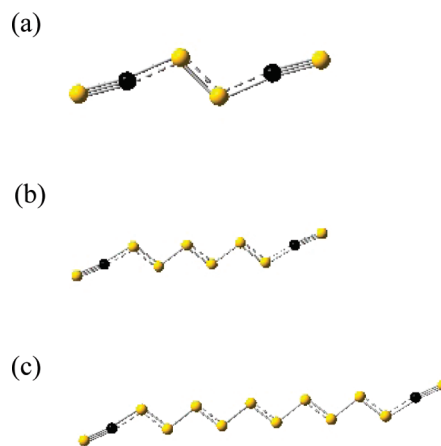
## Introduction

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.<sup>1,2</sup> 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<sup>3–7</sup> 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<sup>7–10</sup> 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<sup>11,12</sup> in the laboratory. More recently, a network polymer of nitrogen has been produced<sup>13</sup> under very high pressure conditions. Experimental successes have sparked theoretical studies<sup>1,14,15</sup> on other potential all-nitrogen molecules. More recent developments include the experimental synthesis of high energy molecules consisting predominantly of nitrogen, including azides<sup>16,17</sup> of various molecules and polyazides<sup>18,19</sup> of atoms and molecules, such as 1,3,5-triazine. Future developments in experiment and theory will further broaden the horizons of high energy nitrogen research.

A recent computational study<sup>20</sup> of isomers of open-chain  $N_4C_2$  showed that the most stable isomer is the one with the carbon atoms occupying the second position from each end of the chain (essentially an azo compound with chain-terminal cyano groups). Compared with its isomers, this so-called “isomer 25” is more stable both thermodynamically and with respect to dissociation. In the current study, these structural ideas are extended to longer chains of nitrogen, which lead to compounds that are even richer in nitrogen than  $N_4C_2$ . Theoretical calculations are made on a series of compounds  $N_xC_2$ , where  $x = 4, 6, 8, 10$ , and 12. Energetic and structural properties of these molecules are calculated and discussed.

## Computational Methods

Geometries and vibrational frequencies of carbon–nitrogen molecules in this study are optimized using the MP2 method,<sup>21</sup>



**Figure 1.** Representative  $N_xC_2$  chains: (a)  $N_4C_2$  (b)  $N_8C_2$  (c)  $N_{12}C_2$ . Nitrogen atoms are shown in yellow, and carbon atoms are shown in black.

with single energy points calculated with coupled-cluster theory<sup>22</sup> (CCSD(T)). The Dunning cc-pVDZ basis set<sup>23</sup> is used for all calculations in this study. Calculations are carried out using the Gaussian03 computational chemistry software<sup>24</sup> (and its Windows counterpart Gaussian03W).

## Results and Discussion

**Structure of  $N_xC_2$  Molecules.** Several representative  $N_xC_2$  open chains are shown in Figure 1. All of the molecules in the  $N_xC_2$  series have  $C_{2h}$  point group symmetry, and the MP2/cc-pVDZ bond lengths for each molecule are shown in Table 1. While the bond lengths for  $N_4C_2$  differ somewhat from other members of the series,  $N_6C_2$  and all longer chains demonstrate a rapid convergence to the structure of the long-chain limit. The bonds of these molecules are of essentially identical length, showing no structural variations with respect to chain length. Presumably all longer molecules in the series would show the same structural features. Regarding the bond lengths themselves, they show evidence of delocalization that results from the conjugation of nitrogen–nitrogen single and double bonds and the chain terminal carbon–nitrogen single and triple bonds. The

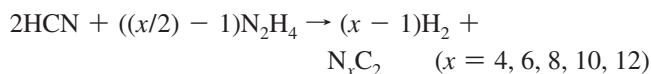
**TABLE 1: Bond Lengths (Å) for Open-Chain Molecules  $N_xC_2$ <sup>a</sup>**

$N_4C_2$	$N_6C_2$	$N_8C_2$	$N_{10}C_2$	$N_{12}C_2$
1.191 (CN)	1.190 (CN)	1.190 (CN)	1.190 (CN)	1.190 (CN)
1.380 (CN)	1.376 (CN)	1.377 (CN)	1.377 (CN)	1.377 (CN)
1.288	1.276	1.277	1.277	1.277
	1.444	1.441	1.442	1.442
		1.268	1.268	1.268
			1.440	1.440
				1.269

<sup>a</sup> Bond lengths are listed from the end of the chain, with carbon–nitrogen (CN) bonds marked as such. All other bonds are nitrogen–nitrogen bonds. Since the molecules have  $C_{2h}$  symmetry, only symmetry-independent bonds are listed.

chain terminal C–N triple bond has a length of 1.190 Å with the MP2/cc-pVDZ method, which is slightly longer than the analogous bond in HCN (1.182 Å) at the same level of theory. The second bond in each chain, formally a C–N single bond, has a length of about 1.38 Å for all  $N_xC_2$  molecules, which is much shorter than the 1.467 Å bond in methylamine. The nitrogen–nitrogen bonds in Table 1 alternate between double and single bond order, and compared with similar bonds in  $N_2H_2$  (N=N 1.266 Å) and hydrazine (N–N 1.481 Å), the double bonds in the  $N_xC_2$  are lengthened and the single bonds are shortened. Delocalization of the conjugated  $\pi$ -bonds is occurring along the entire length of each chain.

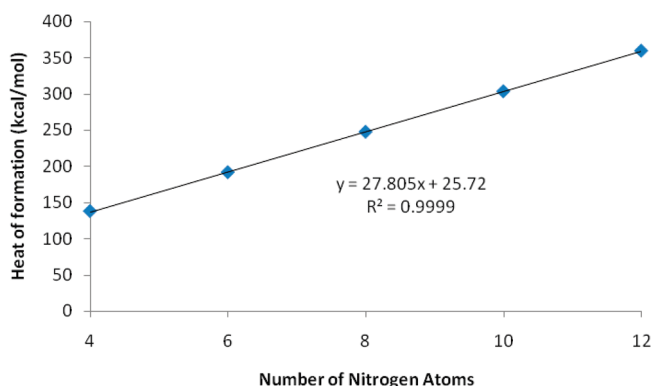
**Energy Properties.** Heats of formation, which indicate the amount of energy each molecule would release upon decomposition, are calculated for each molecule in the  $N_xC_2$  series. The heat of formation values are calculated from the following equation:



Heats of formation values are calculated using CCSD(T)/cc-pVDZ energies for each molecule (at MP2/cc-pVDZ geometries), corrected by zero-point energies calculated from unscaled MP2/cc-pVDZ vibrational frequencies<sup>25</sup> at 0 K. The coupled-cluster calculations all had T1 diagnostic values of 0.015–0.016, which validates the single-reference approach in this study. (Benchmarking this method using a similar equation for NCCN and NCCCCN yields heats of formation of +73.7 and +126.7 kcal/mol, respectively, compared with the experimental values<sup>26</sup> of +73.87 and +127.50 kcal/mol.)

The CCSD(T)/cc-pVDZ heats of formation for the  $N_xC_2$  series of molecules are graphically represented in Figure 2. The series has a strong linear correlation between heat of formation and chain length. The slope of the graph is the additional heat of formation per nitrogen atom as the chain is lengthened, and the intercept of the graph is a constant heat of formation that can be ascribed to chain-terminal effects. The per-nitrogen-atom heat of formation is roughly 28 kcal/mol per atom. Molecules in the series become increasingly energetic with increasing chain length.

**Kinetic Stability.** Do these molecules possess the kinetic stability necessary for high-energy materials? The stability of  $N_4C_2$  has been demonstrated<sup>20</sup> in detail previously, with all likely dissociation pathways going through at least one high-energy step. The key is the chain-terminal CN bonding group. If the molecules had a chain-terminal  $N_2$  group, that  $N_2$  unit would be easily lost, with the release of energy that would tend to

**Figure 2.** Heats of formation of  $N_xC_2$  molecules.**TABLE 2: Energies of Triplets States of  $N_xC_2$ , Relative to the Singlet<sup>a</sup>**

molecule	triplet state	triplet energy
$N_4C_2$	$^3B_g$	+58.4
$N_6C_2$	$^3A_u$	+58.4
$N_8C_2$	$^3B_u$	+94.8
$N_{10}C_2$	$^3B_u$	+97.4
$N_{12}C_2$	$^3B_g$	+110.6

<sup>a</sup> Triplet geometries are calculated with MP2/cc-pVDZ, and the energies are expressed in kcal/mol.

**TABLE 3: Dissociation Energies for the  $N_6C_2$  Open Chain<sup>a</sup>**

reaction	energy
$N_6C_2 \rightarrow NCN_4 + CN$	+103.1
$N_6C_2 \rightarrow NCN_3 + NCN$	+31.1
$N_6C_2 \rightarrow 2 NCN_2$	+39.3

<sup>a</sup> Energies are calculated with the MP2/cc-pVDZ method and are shown in kcal/mol for the products relative to the reactant  $N_6C_2$ .

promote the rapid destruction of the rest of the chain. This has been also been shown in the previous study<sup>20</sup> for the isomer designated “isomer 23”. Because of the chain-terminal CN group, dissociations of the  $N_xC_2$  chains would most likely involve the loss of CN, NCN, or NCNN from the end of the chain. Since all of these are open-shell species, the dissociations cannot readily occur on the singlet potential energy surface. Therefore, dissociation of the chains depends on the accessibility of alternative electronic states. Table 2 shows the results of MP2/cc-pVDZ optimizations to the lowest triplet states of each of the  $N_xC_2$  chains. The energies of the triplet state are all high relative to the singlet, and in fact, they are increasing with increasing chain length. Further, calculations have been carried out on dissociation reactions for the  $N_6C_2$  chain (the kinetic stability of  $N_4C_2$  having been established previously), and the results are shown in Table 3. All first-step dissociations of  $N_6C_2$  are substantially (30–100 kcal/mol) endothermic, which indicates that the molecule has no low-energy paths to dissociation, most likely because the products do not lie on the singlet energy surface. Since all of the longer chains follow similar dissociation paths, the  $N_xC_2$  chains should all have good resistance to dissociation.

## Conclusions

High-energy nitrogen–carbon molecules have been characterized as to their structural and energetic properties. A series of molecules  $N_xC_2$  have been studied and found to demonstrate the following: (1) The energy release properties of the molecules vary linearly with chain length, (2) the molecular structures

demonstrate large effects from conjugation of  $\pi$ -bonds, and (3) the molecules should have favorable kinetic stability as high-energy materials.

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**Supporting Information Available:** Geometries and vibrational frequencies of all  $N_3C_2$  chains. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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