

## Stability and Dissociation Energies of Open-Chain $N_4C_2$

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**Abstract:** Complex forms of nitrogen are of interest due to their potential as high-energy materials. Many forms of nitrogen, including open-chain and cage molecules, have been studied previously. While many all-nitrogen molecules  $N_x$  have been shown to be too unstable for high-energy applications, it has been shown that certain heteroatoms (including carbon) can stabilize a nitrogen structure. A molecule that is not 100% nitrogen will be less energetic, but that energy loss is a tradeoff for the improved stability. In this study, open-chain  $N_4C_2$  (70% nitrogen by mass) isomers are studied by theoretical calculations to determine isomer stability and dissociation energies. Calculations are carried out with density functional theory (PBE1PBE), perturbation theory (MP2), and coupled-cluster theory (CCSD(T)). Trends in stability of the molecules 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.

The stability properties of  $N_x$  molecules have also been extensively studied in a computational survey<sup>20</sup> 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<sup>21</sup> 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<sup>22</sup> 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<sup>23,24</sup> 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  $60^\circ$  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, while it is possible to identify in relative terms which nitrogen cages are the most stable, it has been shown<sup>7</sup>

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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<sup>16–18</sup> cited above, theoretical studies have been carried out that show, for example, that nitrogen cages can be stabilized by oxygen insertion<sup>25,26</sup> or phosphorus substitution.<sup>27</sup>

A study<sup>28</sup> 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  $N_{12}$ . A further study<sup>29</sup> of several isomers of  $N_6C_6H_6$  showed that, for substitutions of C–H bonding groups into an  $N_{12}$  cage, the most stable isomers were the ones with the largest number of C–N bonds. Also, the isomers with the highest number of C–N bonds also had the highest dissociation energies in the N–N bonds, which is significant because the N–N were weaker than other bonds in the cage. The strength of the N–N bonds, therefore, plays a key role in the overall stability of the molecules with respect to dissociation. Similar studies<sup>30</sup> have been carried out for cage isomers of  $N_8C_8H_8$ .

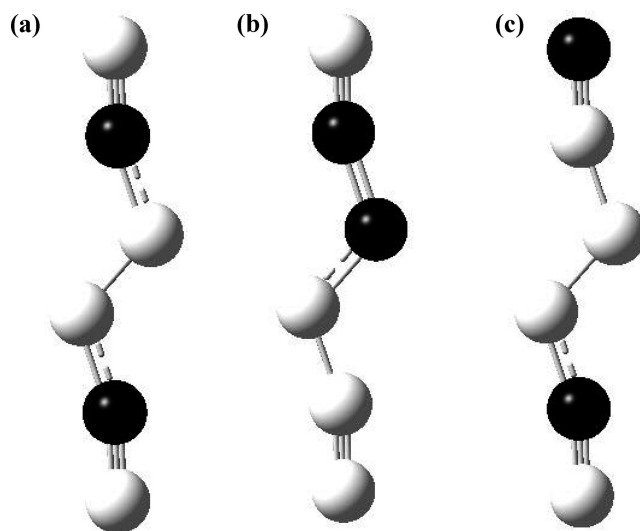
In the current study, a similar idea is applied to open-chain molecules rather than cages. Isomers of open-chain  $N_4C_2$  are studied as two carbon atoms are substituted into the structure of open-chain  $N_6$ . Variations in the placement of the two carbon atoms are considered and discussed. For nomenclature purposes, each isomer shall be named according to the positions of the two carbons. “Isomer 12”, for example, shall refer to a chain of six atoms with positions 1 and 2 occupied by carbon and the rest nitrogen atoms. The energies of these isomers are calculated with respect to each other and with respect to plausible dissociation products, thereby giving a measure of stability with respect to dissociation. Figure 1.

## Computational Methods

Geometries are optimized with second-order Moller–Plesset perturbation theory<sup>31</sup> (MP2) and density functional theory<sup>32</sup> (PBE1PBE). Single energy points are calculated with coupled-cluster theory<sup>33</sup> (CCSD(T)). Each molecule in this study is calculated in its own ground state, which is the singlet for  $N_4C_2$  but not necessarily the singlet for all dissociation products. The correlation-consistent basis sets<sup>34</sup> of Dunning are used, including double- $\zeta$  (cc-pVDZ), augmented double- $\zeta$  (aug-cc-pVDZ), and triple- $\zeta$  (cc-pVTZ). The Gaussian 03 computational chemistry software<sup>35</sup> and Windows counterpart Gaussian 03W are used for the calculations in this study.

## Results and Discussion

**Isomer stability trends.** Open-chain  $N_4C_2$  has nine structural isomers, designated by the carbon positions as isomers 12, 13, 14, 15, 16, 23, 24, 25, and 34, respectively. PBE1PBE, MP2, and CCSD(T) relative energies with the cc-pVDZ for the nine isomers are shown in Table 1. Two



**Figure 1.** (a)  $N_4C_2$  isomer 25 ( $C_{2h}$  point group symmetry). (b)  $N_4C_2$  isomer 23 ( $C_s$  point group symmetry). (c)  $N_4C_2$  isomer 15 ( $C_s$  point group symmetry). Carbon atoms are shown in black; nitrogen atoms are in white.

**Table 1.** PBE1PBE, MP2, and CCSD(T)/MP2 Relative Energies with the cc-pVDZ Basis Set for Isomers of Open-Chain  $N_4C_2$  (Energies in kilocalories/mole)<sup>a</sup>

isomer	PBE1PBE	MP2	CCSD(T)/MP2	carbon charges
25	0.0	0.0	0.0	+0.19, +0.19
23	+28.0	+31.9	+33.2	+0.02, −0.03
15	+29.3	+34.9	+30.2	−0.03, +0.18
34	+34.4	+35.9	+42.6	−0.31, −0.31
13	+42.0	+49.8	+47.7	−0.09, +0.02
14	+43.4	<i>b</i>		−0.11, +0.02
16	+61.4	+71.8	+63.1	−0.04, −0.04
12	+92.0	+106.3	+100.4	−0.15, +0.08
24	<i>b</i>			

<sup>a</sup> Mulliken charges on the carbon atoms are included.  
<sup>b</sup> Optimization was dissociative (loss of  $N_2$ ).

trends in stability appear in the data. The primary trend appears to be a disfavoring of isomers with a carbon atom on the end of the chain. Most of the isomers with a carbon on the end are at the high end of the energy range, and even isomer 15 is much less stable than the structurally similar isomer 25. Mulliken charges shown in Table 1 show a correlation between stability and the charges on the carbon atoms. Carbon bonded to nitrogen will typically take a positive partial charge because of differences in electronegativity, but carbon on the end of the  $N_4C_2$  chain tends to take on a partial negative charge. (If the atom on the end of the chain has a triple bond and a lone pair, this leads to neutral nitrogen but negative carbon.) The positive charges on carbon in isomer 25, and their interactions with neighboring negative nitrogen, stabilize isomer 25 and cause it to be the most stable  $N_4C_2$  chain.

The secondary trend is a disfavoring of isomers with neighboring carbon atoms. Isomers with neighboring carbon atoms have one carbon–carbon bond, two carbon–nitrogen bonds, and two nitrogen–nitrogen bonds. Isomers without neighboring carbon atoms have zero carbon–carbon bonds, four carbon–nitrogen bonds, and one nitrogen–nitrogen

**Table 2.** Cis-Trans Energies for N<sub>4</sub>C<sub>2</sub> Isomers 25, 15, and 16 Calculated with the PBE1PBE/cc-pVDZ Method (Relative Energies in kilocalories/mole)

isomer	trans	cis
25	0.0	+4.3
15	0.0	+2.6
16	0.0	+0.6

bond. Therefore, the introduction of neighboring carbon results in the replacement of two carbon–nitrogen bonds with carbon–carbon and nitrogen–nitrogen bonds. That replacement results in a net reduction in bond enthalpy and a net loss in overall stability. The least stable isomer in this study, isomer 12, has both destabilizing features; one carbon is on the end of the chain, and the two carbon atoms are neighbors.

**Cis–Trans Isomers.** From a chemical point of view, isomers 25, 15, and 16 can be viewed as azo compounds because of the central N–N bonding group, but do these compounds really have the structure of azo compounds? The Lewis diagram of isomer 25, for example, would show a central N=N double bond, C–N single bonds to the azo bonding group, and chain terminal C–N triple bonds in the cyano groups. Modeling these bonds by, respectively, *trans*-N<sub>2</sub>H<sub>2</sub>, methylamine, and HCN yields bond lengths of 1.239 Å for N=N, 1.454 Å for C–N single bond, and 1.156 Å for C–N triple bond, at the PBE1PBE/cc-pVDZ level of theory. The corresponding bond lengths for isomer 25 are 1.259 Å for N=N (slightly elongated), 1.355 Å for C–N single bond (significantly shortened), and 1.165 Å for C≡N triple bond (slightly elongated). Since the shortening of the C–N single bonds is likely the result of resonance delocalization from conjugated  $\pi$ -bonds, the structure of isomer 25 is very consistent with a trans-azo compound with cyano bonding groups.

This opens the possibility of cis–trans isomerism with respect to the cyano and isocyano bonding groups attached to the azo center. All of the energies in Table 1 involve trans isomers of 25, 15, and 16. However, to verify that these trans isomers are the most stable form, cis isomers have been optimized with the PBE1PBE/cc-pVDZ method, and the results are shown in Table 2. The calculations confirm that the trans isomers are, in fact, more stable than their cis counterparts, by an amount of energy that follows the stability of the isomers themselves. The most stable isomer, 25, has a cis–trans gap of 4.3 kcal/mol, whereas the highly unstable isomer 16 has a cis–trans gap of less than 1 kcal/mol.

**What happened to isomer 24?** The arguments in favor of the stability of isomer 25, namely, the lack of chain-terminal carbon and the lack of carbon–carbon bonds, should apply equally well to isomer 24. Yet, no data exists for isomer 24 by reason that its PBE1PBE/cc-pVDZ geometry optimization failed. Since the optimization problem was the uncontrolled lengthening of the bond between atoms 4 and 5, detaching N<sub>2</sub> from the end of the chain, a more detailed study of this bond was conducted. A series of PBE1PBE/cc-pVDZ optimizations was carried out with frozen values for the 4–5 bond ranging from 1.30 to 1.55 Å. The optimized energies from these calculations are comparable to the most stable isomers in this study, but in all cases, the first

**Table 3.** Dissociation Energies of N<sub>4</sub>C<sub>2</sub> Isomer 25 (Energies in kilocalories/mole)

		products		
		NCN <sub>2</sub> + CN	NCN + NCN	CN + CN + N <sub>2</sub>
PBE1PBE	cc-pVDZ	+85.8	+61.0	+87.6
MP2	cc-pVDZ	+110.9	+113.8	+100.4
CCSD(T)/MP2	cc-pVDZ	+83.4	+63.3	+65.7
MP2	aug-cc-pVDZ	+105.6	+117.7	+102.9
CCSD(T)/MP2	aug-cc-pVDZ	+77.5	+65.4	+68.5
MP2	cc-pVTZ	+107.2	+121.0	+104.8
CCSD(T)/MP2	cc-pVTZ	+81.0	+69.9	+71.8

**Table 4.** Dissociation Energies of N<sub>4</sub>C<sub>2</sub> Isomer 23 (Energies in kilocalories/mole)

		Products		
		NC <sub>2</sub> N + N <sub>2</sub>	NC <sub>2</sub> + N <sub>3</sub>	CN + CN + N <sub>2</sub>
PBE1PBE	cc-pVDZ	−87.8	+92.4	+59.6
MP2	cc-pVDZ	−111.8	+129.5	+68.5
CCSD(T)/MP2	cc-pVDZ	−108.0	+93.7	+32.5
MP2	aug-cc-pVDZ	−109.2	+133.1	+71.0
CCSD(T)/MP2	aug-cc-pVDZ	−105.2	+96.1	+35.7
MP2	cc-pVTZ	−109.6	+121.0	+73.2
CCSD(T)/MP2	cc-pVTZ	−106.4	+97.3	+39.3

**Table 5.** Dissociation energies of N<sub>4</sub>C<sub>2</sub> isomer 15 (Energies in kilocalories/mole)

		products		
		NCN <sub>2</sub> + CN	NCN + CN <sub>2</sub>	CN + CN + N <sub>2</sub>
PBE1PBE	cc-pVDZ	+56.5	+59.4	+58.3
MP2	cc-pVDZ	+76.0	+101.5	+65.5
CCSD(T)/MP2	cc-pVDZ	+53.2	+62.8	+35.5
MP2	aug-cc-pVDZ	+70.7	+105.6	+67.9
CCSD(T)/MP2	aug-cc-pVDZ	+47.3	+64.9	+38.3
MP2	cc-pVTZ	+72.6	+109.0	+70.2
CCSD(T)/MP2	cc-pVTZ	+50.5	+69.0	+41.4

derivative of the energy with respect to the 4–5 bond indicated an energetic preference for lengthening. Therefore, in a totally unconstrained optimization, this bond will lengthen indefinitely without finding a bound local minimum.

**Dissociation Energies.** The three most thermodynamically stable isomers, namely 25, 15, and 23, are subjected to dissociation studies, and the results are shown in Tables 3, 4 and 5 for isomers 25, 23, and 15, respectively. (Both binary and trinary dissociations are included, because of completeness and because the CN<sub>3</sub> dissociation product itself dissociated to CN and N<sub>2</sub> anyway upon optimization.) CCSD(T)/MP2 predicts lower dissociation energies than MP2, and in most cases, basis set effects cause small increases in dissociation energy. Generally speaking, the PBE1PBE dissociation energies are more accurate than MP2, as compared to CCSD(T). Isomer 23 has a very exothermic dissociation (N<sub>4</sub>C<sub>2</sub> → NC<sub>2</sub>N + N<sub>2</sub>) whereby the molecule loses N<sub>2</sub> from the end of the chain. This behavior is similar to previously studied behavior of all-nitrogen chains. All-nitrogen chains lose N<sub>2</sub> very easily, which is why they are kinetically unstable. Isomer 23 is similarly unstable with



**Table 6.** PBE1PBE/cc-pVDZ Detonation Energies for N<sub>4</sub>C<sub>2</sub> Isomers 25, 23, and 15

isomer	energy (kcal/mol)	energy (kcal/g)
25	132.9	1.66
23	161.0	2.01
15	162.3	2.03

respect to dissociation and is therefore not likely to hold promise as a high-energy material.

Isomers 25 and 15 have dissociation processes that are all endothermic, meaning that these molecules have more resistance to dissociation than isomer 23. For isomer 15, the lowest energy dissociation involves the loss of one or both CN units from the end of the molecule. CCSD(T)/MP2 predicts that dissociation of isomer 15 costs at least 40–50 kcal/mol of energy, and therefore, isomer 15 may have potential as high-energy material. The stability of isomer 25 is even greater than that of isomer 15, with all dissociations requiring at least 70 kcal/mol at the CCSD(T)/cc-pVTZ level of theory. Because of the structural similarities between isomers 25 and 15, most of the dissociation products are the same for the two molecules. The greater kinetic stability of isomer 25 versus isomer 15, reflected in Tables 2 and 3, is a direct result of the greater thermodynamic stability shown in Table 1.

**Detonation Energies.** Detonation energies of the molecules are calculated<sup>36</sup> as the energy released by the reaction  $\text{N}_4\text{C}_2 \rightarrow 2\text{N}_2 + 2\text{C}$  (graphite). Since N<sub>2</sub> and graphitic carbon are the most stable allotropes of the products, these detonation energies also indicate the heats of formation of the N<sub>4</sub>C<sub>2</sub> chains. The energies for isomers 25, 23, and 15 are shown in Table 6. Since all these reactions lead to the same products, the differences in energy are the same as the differences in stability shown in Table 1. A CCSD(T)/cc-pVDZ estimate, based on the model reaction  $2\text{HCN} + \text{N}_2\text{H}_4 \rightarrow 3\text{H}_2 + \text{N}_4\text{C}_2$ , of the heat of formation<sup>37</sup> of isomer 25 predicts a value of 154 kcal/mol, as compared with the 133 kcal/mol in Table 6, possibly indicating that the values in Table 6 are underestimating the detonation energy.

Since isomer 25 has the lowest energy (most stable) to start with, it has the lowest energy of detonation. According to Table 6, isomer 25 has the ability to release about 1.7 kcal/g, while isomers 23 and 15 have an energy release of about 2 kcal/g. The energy release occurs principally because of the formation of N<sub>2</sub>, so the fact that the molecules are 70% nitrogen by mass is a favorable energetic property. These detonation energies are comparable to, for example, the previously studied N<sub>6</sub>C<sub>6</sub>H<sub>6</sub> cages.<sup>29</sup> The difference between these open chains and previously studied cages is that the cages have single bonds, whereas the open chains have double and triple bonds, which are less energetic upon decomposition to N<sub>2</sub>. That is why open chains that are 70% nitrogen have about the same detonation energy as cages that are slightly more than 50% nitrogen. If stable open

chains can be found that are even richer in nitrogen, the energetic properties will improve accordingly.

## Conclusion

N<sub>4</sub>C<sub>2</sub> is an example of a carbon-substituted nitrogen chain that could hold promise as a high-energy material, but there are important considerations in the design of such a molecule for optimal high-energy properties. Carbon atoms should be distributed along a chain such that no C–C bonds occur, but the carbon atoms should not occupy chain-terminal positions. On the other hand, chain-terminal N<sub>2</sub> is likely to be easily lost from a chain, so the best arrangement of carbon atoms would include carbon atoms at the second position with respect to each end of the chain (as seen in isomer 25). N<sub>4</sub>C<sub>2</sub> is 70% nitrogen by mass and has favorable energetic properties. Longer chains that are richer in nitrogen will be even better energetic materials, if they are stable.

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**Supporting Information Available:** PBE1PBE/cc-pVDZ energies and geometries, as well as structural parameters and singlet–triplet excitation energies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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