Research Article

Effect of C–O Bonding on the Stability and Energetics of High-Energy Nitrogen-Carbon Molecules $N_{10}C_2$ and $N_{16}C_2$

Douglas L. Strout

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

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

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Molecules consisting of nitrogen have been the subject of much attention due to their potential as high-energy materials. Decomposition reactions of the type $N_x \rightarrow (x/2)N_2$ can be exothermic by up to 50 kcal/mol per nitrogen atom (approximately 3.5 kilocalories per gram of material). Experimental synthetic successes in high-energy nitrogen materials include the $N_5^+$ and $N_5^-$ ions [1–4] as well as various azido compounds [5–9] and even a network polymer of nitrogen [10]. Additionally, nitrogen-rich salts [11] and the $N_2O^+$ ion [12] have been achieved experimentally. The production of such a diverse group of nitrogen systems demonstrates the potential for such materials as novel high-energy molecules. Nitrogen-based energetic systems have also been the subject of much theoretical research. Theoretical studies of high-energy nitrogen include cyclic and acyclic compounds [13–20], as well as nitrogen cages [21–27]. Structures and thermodynamics of energetic nitrogen systems have been calculated for both small molecules and larger structures with up to seventy-two atoms.

Theoretical studies [28] of cage isomers of $N_{24}$, $N_{30}$, and $N_{36}$ showed that the most stable isomers are narrow cylindrical structures consisting of bands of hexagons capped by triangle-pentagon endcaps in either $D_{3d}$ or $D_{5h}$ point group symmetry. A previous study [29] of molecules of $N_{22}C_2$ showed that the most stable isomer has a $C_2$ parallel to the long axis of the molecule, which allows the $C_2$ unit and its C=C double bond the most planar, ethylene-like environment. The least stable isomers have the $C_2$ unit in proximity to the triangular endcaps, where angle strain around the C=C double bond becomes a destabilizing factor. In the current study, the smaller analogues $N_{10}C_2$ and $N_{16}C_2$ are considered, with the bonding groups $O_3$ and $CO_3$ added to the C=C double bond. The addition of $O_3$ to C=C double bonds in cage molecules such as fullerenes is already well known [30], and the $CO_3$ bonding group could be achieved by reaction with the metastable carbon trioxide molecule [31] or other means involving carbon dioxide and oxygen. These bonding groups are chosen to determine the effects of C–O bonding on nitrogen-carbon molecules. The effects of these bonding groups on the relative isomer energies and on the heat of formation of the molecules are calculated and discussed.

1. Introduction

Molecules consisting entirely or predominantly of nitrogen have been the subject of much research because of their potential as high-energy materials. Decomposition reactions of the type $N_x \rightarrow (x/2)N_2$ can be exothermic by up to 50 kcal/mol per nitrogen atom (approximately 3.5 kilocalories per gram of material). Experimental synthetic successes in high-energy nitrogen materials include the $N_5^+$ and $N_5^-$ ions [1–4] as well as various azido compounds [5–9] and even a network polymer of nitrogen [10]. Additionally, nitrogen-rich salts [11] and the $N_2O^+$ ion [12] have been achieved experimentally. The production of such a diverse group of nitrogen systems demonstrates the potential for such materials as novel high-energy molecules. Nitrogen-based energetic systems have also been the subject of much theoretical research. Theoretical studies of high-energy nitrogen include cyclic and acyclic compounds [13–20], as well as nitrogen cages [21–27]. Structures and thermodynamics of energetic nitrogen systems have been calculated for both small molecules and larger structures with up to seventy-two atoms.

Theoretical studies [28] of cage isomers of $N_{24}$, $N_{30}$, and $N_{36}$ showed that the most stable isomers are narrow cylindrical structures consisting of bands of hexagons capped by triangle-pentagon endcaps in either $D_{3d}$ or $D_{5h}$ point group symmetry. A previous study [29] of molecules of $N_{22}C_2$ showed that the most stable isomer has a $C_2$ parallel to the long axis of the molecule, which allows the $C_2$ unit and its C=C double bond the most planar, ethylene-like environment. The least stable isomers have the $C_2$ unit in proximity to the triangular endcaps, where angle strain around the C=C double bond becomes a destabilizing factor. In the current study, the smaller analogues $N_{10}C_2$ and $N_{16}C_2$ are considered, with the bonding groups $O_3$ and $CO_3$ added to the C=C double bond. The addition of $O_3$ to C=C double bonds in cage molecules such as fullerenes is already well known [30], and the $CO_3$ bonding group could be achieved by reaction with the metastable carbon trioxide molecule [31] or other means involving carbon dioxide and oxygen. These bonding groups are chosen to determine the effects of C–O bonding on nitrogen-carbon molecules. The effects of these bonding groups on the relative isomer energies and on the heat of formation of the molecules are calculated and discussed.

2. Computational Methods

Geometries for all molecules in this study are optimized by the Hartree-Fock method, and Hartree-Fock vibrational frequencies are used to confirm each structure as a local minimum. Single energy points are calculated with
coupled-cluster theory [32, 33] (CCSD(T)). Hartree-Fock method is chosen for geometry optimization for two reasons: (1) previous calculations on nitrogen cages have shown that energy results are insensitive to the choice of optimized geometry and (2) other optimization methods, such as density functional theory, have been shown to be dissociative for certain nitrogen cages. The correlation-consistent cc-pVDZ atomic orbital basis set [34] of Dunning is used for all calculations in this study. Calculations have been carried out using the Gaussian 09 computational chemistry software [35].

3. Results and Discussion

3.1. $\text{N}_{10}\text{C}_2$. The $\text{N}_{10}\text{C}_2$ cage has three isomers, which are shown in Figure 1. These isomers are labeled A, B, and C and represent the three symmetry-independent substitutions of a $\text{C}_2$ unit into the structure of the $\text{N}_{12}$ cage in $D_{3d}$ symmetry. The $\text{O}_3$ and $\text{CO}_3$ adducts of each of these isomers are shown in Figure 2. Energies and vibrational frequencies have been calculated for each molecule, and the energies are shown in Table 1. For $\text{N}_{10}\text{C}_2$, isomer C has the lowest energy, mainly because of angle strain in the triangular endcaps since isomers A and B have at least one carbon atom in the triangle. However, the application of either $\text{O}_3$ or $\text{CO}_3$ bonding group causes a reversal, and isomer B becomes most stable. This is because the addition of $\text{O}_3$ or $\text{CO}_3$ converts the $\text{sp}^2$-hybridized carbon to $\text{sp}^3$, which relieves the ring strain to some extent. It is likely that the isomer A adducts also benefit from the adduct stabilization, but this cannot be confirmed since isomer A of $\text{N}_{10}\text{C}_2$ is not a local minimum on the potential energy surface.

What effect does the addition of $\text{O}_3$ or $\text{CO}_3$ have on the overall energetic properties of the molecules? Nitrogen-carbon cages tend to be highly energetic and have high heat of formation, but molecules with $\text{C}-\text{O}$ bonds tend to have lower heat of formation (the heat of formation [36] of carbon dioxide, e.g., is $-94.0$ kcal/mol). Enthalpies of formation for

TABLE 1: Relative isomer energies (in kcal/mol) for $\text{N}_{10}\text{C}_2$ and its $\text{O}_3$ and $\text{CO}_3$ adducts. Energies calculated with CCSD(T)/cc-pVDZ method. Except where noted, all molecules are local minima confirmed by HF/cc-pVDZ vibrational frequencies.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Isomer A</th>
<th>Isomer B</th>
<th>Isomer C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{N}_{10}\text{C}_2$</td>
<td>Not minimum</td>
<td>+10.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$\text{N}_{10}\text{C}_2\text{O}_3$</td>
<td>+9.3</td>
<td>−4.2</td>
<td>0.0</td>
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<td>+11.2</td>
<td>−5.9</td>
<td>0.0</td>
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</tbody>
</table>

TABLE 2: Enthalpies of formation (in kcal/mol and kcal/g) for $\text{N}_{10}\text{C}_2$ and its $\text{O}_3$ and $\text{CO}_3$ adducts. Energies calculated with CCSD(T)/cc-pVDZ method.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\Delta H_f$ (kcal/mol)</th>
<th>$\Delta H_f$ (kcal/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{N}_{10}\text{C}_2$ ($M = 164$ g/mole)</td>
<td>Isomer A</td>
<td>Isomer B</td>
</tr>
<tr>
<td>Isomer A</td>
<td>Not minimum</td>
<td>+528.3</td>
</tr>
<tr>
<td>Isomer B</td>
<td>+518.3</td>
<td>+3.16</td>
</tr>
<tr>
<td>Isomer C</td>
<td>+518.3</td>
<td>+3.16</td>
</tr>
<tr>
<td>$\text{N}_{10}\text{C}_2\text{O}_3$ ($M = 212$ g/mole)</td>
<td>Isomer A</td>
<td>Isomer B</td>
</tr>
<tr>
<td>Isomer A</td>
<td>+458.9</td>
<td>+2.16</td>
</tr>
<tr>
<td>Isomer B</td>
<td>+445.4</td>
<td>+2.10</td>
</tr>
<tr>
<td>Isomer C</td>
<td>+449.6</td>
<td>+2.12</td>
</tr>
<tr>
<td>$\text{N}_{10}\text{C}_2\text{CO}_3$ ($M = 224$ g/mole)</td>
<td>Isomer A</td>
<td>Isomer B</td>
</tr>
<tr>
<td>Isomer A</td>
<td>+338.2</td>
<td>+1.51</td>
</tr>
<tr>
<td>Isomer B</td>
<td>+321.1</td>
<td>+1.43</td>
</tr>
<tr>
<td>Isomer C</td>
<td>+327.0</td>
<td>+1.46</td>
</tr>
</tbody>
</table>

$\text{N}_{10}\text{C}_2$ and its $\text{O}_3$ and $\text{CO}_3$ adducts are shown in Table 2 and have been calculated using CCSD(T)/cc-pVDZ energies for the following chemical reactions:

$\text{N}_{10}\text{C}_2 + 2\text{O}_2 \rightarrow 5\text{N}_2 + 2\text{CO}_2$

$\text{N}_{10}\text{C}_2\text{O}_3 + \left(\frac{1}{2}\right)\text{O}_2 \rightarrow 5\text{N}_2 + 2\text{CO}_2$

$\text{N}_{10}\text{C}_2\text{CO}_3 + \left(\frac{3}{2}\right)\text{O}_2 \rightarrow 5\text{N}_2 + 3\text{CO}_2$
Figure 2: Adducts of N\textsubscript{10}C\textsubscript{2}: (a) isomer A + O\textsubscript{3}, (b) isomer B + O\textsubscript{3}, (c) isomer C + O\textsubscript{3}, (d) isomer A + CO\textsubscript{3}, (e) isomer B + CO\textsubscript{3}, and (f) isomer C + CO\textsubscript{3}. Nitrogen atoms are shown in yellow, carbon atoms in black, and oxygen atoms in red.

The results in Table 2 show that N\textsubscript{10}C\textsubscript{2} is highly energetic, with a heat of formation above 3.0 kilocalories per gram of material. Such molecules would release a large amount of energy upon their decomposition. Introduction of the O\textsubscript{3} bonding group lowers the heat of formation to about 2.1 kilocalories per gram, and CO\textsubscript{3} lowers the energy even further, down to about 1.5 kilocalories per gram, which is still greater than the energy densities [37] of conventional explosives such as RDX and HMX, which are approximately 0.5–1.0 kcal/g. By the choice of adduct bonding group, the energetic properties of these molecules are essentially tunable, and the tradeoff between stability and energy release may be a significant consideration in the synthesis of these molecules.

3.2. N\textsubscript{16}C\textsubscript{2}. The N\textsubscript{16}C\textsubscript{2} cage has four isomers, which are shown in Figure 3. These isomers are labeled A, B, C, and D and represent the four symmetry-independent substitutions of a C\textsubscript{2} unit into the structure of the N\textsubscript{18} cage in D\textsubscript{3h} symmetry. The O\textsubscript{3} and CO\textsubscript{3} adducts of the four isomers are shown in Figure 4. Energies and vibrational frequencies have been calculated for each molecule, and the energies are shown in Table 3. For N\textsubscript{16}C\textsubscript{2}, isomer D is easily the most stable. Isomer D has a C\textsubscript{2} unit parallel to the C\textsubscript{3} axis of the molecule, and the arrangement of the four nitrogen atoms around the C\textsubscript{2} unit in isomer D provides an environment much closer to the planar “ethylene-like” geometry preferred by sp\textsuperscript{2}-hybridized carbon atoms. Isomers A, B, and C all have a C\textsubscript{2} unit with significant angle strain or significant twisting of the four nitrogen atoms around the C\textsubscript{2}. By contrast, N\textsubscript{16}C\textsubscript{2} does not have this very stable isomer, which explains why N\textsubscript{16}C\textsubscript{2} has isomer energies much closer together than does N\textsubscript{10}C\textsubscript{2}. N\textsubscript{16}C\textsubscript{2} isomers show a rapid increase in energy as the C\textsubscript{2} is located closer to the triangular endcaps. In a manner similar to N\textsubscript{10}C\textsubscript{2}, the adduct energies in Table 3 show a substantial narrowing of the energy gaps between isomers, because of the relief of angle strain in isomers A and B. However, owing to the special stability of isomer D, the relief of ring strain does not cause a reversal of the ordering of the isomer energies.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Isomer A</th>
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<th>Isomer C</th>
<th>Isomer D</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{16}C\textsubscript{2}</td>
<td>Not minimum</td>
<td>+65.3</td>
<td>+28.8</td>
<td>0.0</td>
</tr>
<tr>
<td>N\textsubscript{16}C\textsubscript{2}O\textsubscript{3}</td>
<td>+40.5</td>
<td>+21.8</td>
<td>+9.3</td>
<td>0.0</td>
</tr>
<tr>
<td>N\textsubscript{16}C\textsubscript{2}CO\textsubscript{3}</td>
<td>+43.2</td>
<td>+20.6</td>
<td>+11.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
The first interesting result shown in Table 4 is that the N\textsubscript{16}C\textsubscript{2} isomers have enthalpies of formation that are no higher than the corresponding isomers of N\textsubscript{10}C\textsubscript{2} (about 3.0 kilocalories per gram), despite the fact that N\textsubscript{16}C\textsubscript{2} has a higher proportionate nitrogen content. It appears that the increased size of the molecule, and correspondingly greater distance between the triangular endcaps, provides for a more relaxed, less strained structure that stabilizes the molecule. On the other hand, the higher nitrogen content of N\textsubscript{16}C\textsubscript{2} does have an impact on the heat of formation of the N\textsubscript{16}C\textsubscript{2} adducts. Whereas N\textsubscript{10}C\textsubscript{2} and N\textsubscript{16}C\textsubscript{2} have about the same heat of formation, N\textsubscript{16}C\textsubscript{2}O\textsubscript{3} and N\textsubscript{16}C\textsubscript{2}CO\textsubscript{3} have much higher heat of formation than their smaller counterparts. N\textsubscript{16}C\textsubscript{2}O\textsubscript{3} isomers have a heat of formation of 2.3–2.5 kilocalories per gram, and N\textsubscript{16}C\textsubscript{2}CO\textsubscript{3} has heat of formation of 1.9–2.0 kilocalories per gram. As with N\textsubscript{10}C\textsubscript{2}, N\textsubscript{16}C\textsubscript{2} shows a variability of energetic properties depending on the nature of the bonding group added to the C=C double bond.

4. Conclusion

N\textsubscript{10}C\textsubscript{2} and N\textsubscript{16}C\textsubscript{2} are high-energy molecules whose properties can be varied by the addition of various bonding groups to the C=C double bond. Adducts of both N\textsubscript{10}C\textsubscript{2} and N\textsubscript{16}C\textsubscript{2} demonstrate changes in energetic properties that reflect both relief of ring strain with the structure and the stabilizing influence of the carbon-oxygen bond. The stability and energy-release properties of these molecules can be adjusted by the appropriate choice of adduct bonding group, which should provide a number of potential synthetic targets. Further studies involving multiple C\textsubscript{2} units in the structure and additional choices of adduct bonding group should reveal additional molecules with potential as high-energy materials.
Figure 4: Adducts of $\text{N}_{16}\text{C}_{2}$: (a) isomer $\text{A} + \text{O}_3$, (b) isomer $\text{B} + \text{O}_3$, (c) isomer $\text{C} + \text{O}_3$, (d) isomer $\text{D} + \text{O}_3$, (e) isomer $\text{A} + \text{CO}_3$, (f) isomer $\text{B} + \text{CO}_3$, (g) isomer $\text{C} + \text{CO}_3$, and (h) isomer $\text{D} + \text{CO}_3$. Nitrogen atoms are shown in yellow, carbon atoms in black, and oxygen atoms in red.
Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

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References


[4] D. A. Dixon, D. Feller, K. O. Christe et al., “Enthalpies of formation of gas-phase N\textsubscript{5}, N\textsubscript{5}⁺, N\textsubscript{5}²⁺, and N\textsubscript{5}⁻ from Ab Initio molecular orbital theory, stability predictions for N\textsubscript{5}⁺ N\textsubscript{5}, N\textsubscript{5}⁺N\textsubscript{5}, and experimental evidence for the instability of N\textsubscript{5}⁺N\textsubscript{5}⁺,” Journal of the American Chemical Society, vol. 126, no. 3, pp. 834–843, 2004.


[6] R. Haiges, S. Schneider, T. Schroer, and K. O. Christe, “High-Energy-Density Materials: Synthesis and Characterization of N\textsubscript{5}⁺[P(N\textsubscript{5})\textsubscript{4}], N\textsubscript{5}⁺[B(N\textsubscript{5})\textsubscript{4}], N\textsubscript{5}⁺[HF\textsubscript{5}], n·HF, N\textsubscript{5}⁺[BF\textsubscript{5}], N\textsubscript{5}⁺[PF\textsubscript{5}], and N\textsubscript{5}⁺[SO\textsubscript{2}F\textsubscript{2}]” Angewandte Chemie International Edition, vol. 43, pp. 4919–4924, 2004.


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