Research Article

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

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Received 19 May 2014; Accepted 4 December 2014; Published 25 December 2014

Academic Editor: Mohamed Sarakha

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Molecules consisting of nitrogen have been the subject of much attention due to their potential as high-energy materials. Complex molecules consisting entirely of nitrogen can be subject to rapid decomposition, and therefore other atoms are incorporated into the structure to enhance stability. Previous studies have explored the incorporation of carbon atoms into otherwise all-nitrogen cages molecules. The current study involves two such cages, $N_{10}C_2$ and $N_{16}C_2$, whose structures are derived from N_{12} and N_{18} , respectively. The $N_{10}C_2$ and $N_{16}C_2$ cages in this study are modified by bonding groups O_3 and CO_3 to determine the effect on the relative energies between the isomers and on the thermodynamic energy release properties. Energetic trends for $N_{10}C_2$ and $N_{16}C_2$ 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_7O^+ 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_{3h} 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

FIGURE 1: Isomers of $N_{10}C_2$: (a) isomer A, (b) isomer B, and (c) isomer C. Nitrogen atoms are shown in yellow, carbon atoms in black.

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. $N_{10}C_2$. The $N_{10}C_2$ 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 C_2 unit into the structure of the N_{12} cage in D_{3d} symmetry. The O_3 and 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 $N_{10}C_2$, 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 O_3 or CO_3 bonding group causes a reversal, and isomer B becomes most stable. This is because the addition of O_3 or CO_3 converts the sp^2 -hybridized carbon to 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 $N_{10}C_2$ is not a local minimum on the potential energy surface.

What effect does the addition of O_3 or 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 C–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 $N_{10}C_2$ and its O_3 and 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.

	Isomer A	Isomer B	Isomer C
$N_{10}C_2$	Not minimum	+10.0	0.0
$N_{10}C_2O_3$	+9.3	-4.2	0.0
$N_{10}C_2CO_3$	+11.2	-5.9	0.0

TABLE 2: Enthalpies of formation (in kcal/mol and kcal/g) for $N_{10}C_2$ and its O_3 and CO_3 adducts. Energies calculated with CCSD(T)/cc-pVDZ method.

		ΔH_f (kcal/mol)	ΔH_f (kcal/g)
$N_{10}C_2$ ($M = 164$ g/mole)	Isomer A	Not minimum	Not minimum
	Isomer B	+528.3	+3.22
	Isomer C	+518.3	+3.16
$N_{10}C_2O_3$ ($M = 212$ g/mole)	Isomer A	+458.9	+2.16
	Isomer B	+445.4	+2.10
	Isomer C	+449.6	+2.12
$N_{10}C_2CO_3$ ($M = 224$ g/mole)	Isomer A	+338.2	+1.51
	Isomer B	+321.1	+1.43
	Isomer C	+327.0	+1.46

$N_{10}C_2$ and its O_3 and CO_3 adducts are shown in Table 2 and have been calculated using CCSD(T)/cc-pVDZ energies for the following chemical reactions:

FIGURE 2: Adducts of $N_{10}C_2$: (a) isomer A + O_3 , (b) isomer B + O_3 , (c) isomer C + O_3 , (d) isomer A + CO_3 , (e) isomer B + CO_3 , and (f) isomer C + CO_3 . Nitrogen atoms are shown in yellow, carbon atoms in black, and oxygen atoms in red.

The results in Table 2 show that $N_{10}C_2$ 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_3 bonding group lowers the heat of formation to about 2.1 kilocalories per gram, and CO_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. $N_{16}C_2$. The $N_{16}C_2$ 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_2 unit into the structure of the N_{18} cage in D_{3h} symmetry. The O_3 and CO_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 $N_{16}C_2$, isomer D is easily the most stable. Isomer D has a C_2 unit parallel to the C_3 axis of the molecule, and the arrangement of the four nitrogen atoms around the C_2 unit in isomer D provides an environment much

TABLE 3: Relative isomer energies (in kcal/mol) for $N_{16}C_2$ and its O_3 and 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.

	Isomer A	Isomer B	Isomer C	Isomer D
$N_{16}C_2$	Not minimum	+65.3	+28.8	0.0
$N_{16}C_2O_3$	+40.5	+21.8	+9.3	0.0
$N_{16}C_2CO_3$	+43.2	+20.6	+11.0	0.0

closer to the planar “ethylene-like” geometry preferred by sp^2 -hybridized carbon atoms. Isomers A, B, and C all have a C_2 unit with significant angle strain or significant twisting of the four nitrogen atoms around the C_2 . By contrast, $N_{10}C_2$ does not have this very stable isomer, which explains why $N_{10}C_2$ has isomer energies much closer together than does $N_{16}C_2$. $N_{16}C_2$ isomers show a rapid increase in energy as the C_2 is located closer to the triangular endcaps. In a manner similar to $N_{10}C_2$, 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.

FIGURE 3: Isomers of $N_{16}C_2$: (a) isomer A, (b) isomer B, (c) isomer C, and (d) isomer D. Nitrogen atoms are shown in yellow, carbon atoms in black.

TABLE 4: Enthalpies of formation (in kcal/mol and kcal/g) for $N_{16}C_2$ and its O_3 and CO_3 adducts. Energies calculated with CCSD(T)/cc-pVDZ method.

		ΔH_f (kcal/mol)	ΔH_f (kcal/g)
$N_{16}C_2$ ($M = 248$ g/mole)	Isomer A	Not minimum	Not minimum
	Isomer B	+800.1	+3.23
	Isomer C	+763.6	+3.08
	Isomer D	+734.8	+2.96
$N_{16}C_2O_3$ ($M = 296$ g/mole)	Isomer A	+740.9	+2.50
	Isomer B	+722.2	+2.44
	Isomer C	+709.7	+2.40
	Isomer D	+700.4	+2.37
$N_{16}C_2CO_3$ ($M = 308$ g/mole)	Isomer A	+619.9	+2.01
	Isomer B	+597.3	+1.94
	Isomer C	+587.7	+1.91
	Isomer D	+576.7	+1.87

Enthalpies of formation for $N_{16}C_2$ and its O_3 and CO_3 adducts are shown in Table 4 and have been calculated using CCSD(T)/cc-pVDZ energies for the following chemical reactions:

The first interesting result shown in Table 4 is that the $N_{16}C_2$ isomers have enthalpies of formation that are no higher than the corresponding isomers of $N_{10}C_2$ (about 3.0 kilocalories per gram), despite the fact that $N_{16}C_2$ 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 $N_{16}C_2$ does have an impact on the heat of formation of the $N_{16}C_2$ adducts. Whereas $N_{10}C_2$ and $N_{16}C_2$ have about the same heat of formation, $N_{16}C_2O_3$ and $N_{16}C_2CO_3$ have much higher heat of formation than their smaller counterparts. $N_{16}C_2O_3$ isomers have a heat of formation of 2.3–2.5 kilocalories per gram, and $N_{16}C_2CO_3$ has heat of formation of 1.9–2.0 kilocalories per gram. As with $N_{10}C_2$, $N_{16}C_2$ shows a variability of energetic properties depending on the nature of the bonding group added to the C=C double bond.

4. Conclusion

$N_{10}C_2$ and $N_{16}C_2$ 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 $N_{10}C_2$ and $N_{16}C_2$ 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_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 $N_{16}C_2$: (a) isomer A + O_3 , (b) isomer B + O_3 , (c) isomer C + O_3 , (d) isomer D + O_3 , (e) isomer A + CO_3 , (f) isomer B + CO_3 , (g) isomer C + CO_3 , and (h) isomer D + 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.

Acknowledgments

The Alabama Supercomputer Authority is gratefully acknowledged for a grant of computer time on the SGI Ultraviolet in Huntsville, AL. This work was supported by the National Science Foundation (NSF/HBCU-UP Grant 0505872). This work was also supported by the National Institutes of Health (NIH/NCMHD 1P20MD000547-01) 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.

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