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Metal-Ion Binding to High-Energy $N_{12}C_4$

Kasha Casey, Jessica Thomas, Zamyra Lambert, and Douglas L. Strout*

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

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Carbon−nitrogen compounds are of interest for their potential as high-energy materials. One major issue in determining the structures of high-energy materials is molecular stability; a more stable energetic compound is more likely to be useful in a wider variety of applications. In this study, binding energies are calculated for a high-energy $N_{12}C_4$ structure with a series of metal ions to determine preferred binding sites. A metal ion bound to the molecule at a preferred site may stabilize the molecule and render it more potentially useful. The results are calculated on using the PBE1PBE density functional method with the cc-pVDZ basis set of Dunning. Trends in binding energies are calculated and discussed with respect to both the identity of the ion and the various binding sites on the $N_{12}C_4$ molecule.

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.[1,2] 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[3−7] have shown that numerous N_x molecules are not sufficiently stable to be practical HEDM, including cyclic and acyclic isomers with 8 to 12 atoms. Cage isomers of N_8 and N_{12} have also been shown[7−10] 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[11,12] in the laboratory. More recently, a network polymer of nitrogen has been produced[13] under very high pressure conditions. Experimental successes have sparked theoretical studies[1,14,15] on other potential all-nitrogen molecules. More recent developments include the experimental synthesis of high-energy molecules consisting predominantly of nitrogen, including azides[16,17] of various molecules and polyazides[18,19] 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[20] 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[21] 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[22] 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[23,24] 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° 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, whereas it is possible to identify in relative terms which nitrogen cages are the most stable, it has been shown[7] 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[16−18] cited above, theoretical studies have been carried out that show, for example, that nitrogen cages can be stabilized by oxygen insertion[25,26] or phosphorus substitution.[27]

Carbon−nitrogen cages have also been extensively studied,[28−31] including their interactions with metal ions.[32] Cage isomers of $N_{10}C_{10}H_{10}$ and $N_{12}C_{12}H_{12}$ were optimized and compared based on both their structural properties and their ability to accommodate endohedral metal cations. The impact of the ions on cage stability was found to depend on two factors: (1) The shape of the interior cavity of the cage, and (2) the proximity of negatively polarized nitrogen atoms to the body center occupied by the cation. A previous study[33] of cyclic carbon−nitrogen molecules demonstrated the stability of a cyclic N_6C_2 molecule with two nitrogen atoms bonded to an N_4C_2 hexagon. In the current study, a 3D dimer ($N_{12}C_4$) of this molecule is studied to determine its stability properties. The structure of this molecule is analyzed in detail, and the molecule's ability to bind small metal ions is also calculated and discussed. Binding energies for Li^+, Be^{2+}, Na^+, and Mg^{2+} for various binding sites on the $N_{12}C_4$ structure are calculated to determine preferred binding for each ion.

Computational Methods

The PBE1PBE and B3LYP density functional methods[34,35] are used for geometry optimizations of $N_{12}C_4$ and $MN_{12}C_4$ (M = metal ion). The correlation-consistent basis sets[36] of Dunning are used. The *Gaussian03* computational chemistry software[37]

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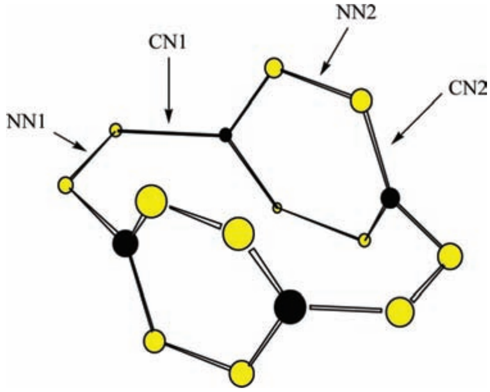

Figure 1. $N_{12}C_4$ molecule (D_{2h} symmetry point group). Symmetry-independent bonds are labeled. Carbon atoms are shown in black, and nitrogen atoms are shown in yellow.

TABLE 1: Bond Lengths of $N_{12}C_4$, Calculated with PBE1PBE/cc-pVDZ

bond	length
CN1	1.433 Å
CN2	1.335 Å
NN1	1.249 Å
NN2	1.315 Å
C−N bond of CH_3NH_2	1.454 Å
C═N bond of CH_2NH	1.268 Å
N═N bond of N_2H_2	1.238 Å

(along with Windows counterpart *Gaussian03W*) is used for all calculations in this study. Counterpoise calculations are carried out for all $MN_{12}C_4$ systems to determine the magnitude of basis set superposition error (BSSE).

Results and Discussion

The structure of $N_{12}C_4$ is shown in Figure 1. The molecule is a dimer of the previously studied[33] N_6C_2, and the $N_{12}C_4$ has four symmetry-independent bonds in D_{2h} point group symmetry. The four bonds are labeled NN1, NN2, CN1, and CN2, and their PBE1PBE/cc-pVDZ bond lengths are shown in Table 1 along with bond lengths from small model molecules chosen to give representative bond lengths for the C−N single bond, C−N double bond, and N−N double bond. The bond lengths shed light on the bonding properties of the $N_{12}C_4$ structure. The bonds of the hexagons, namely CN2 and NN2, have bond lengths indicative of an aromatic ring. CN2 has a bond length, 1.335 Å, roughly halfway between single bond and double bond length. The NN2 bond is much longer than the representative N−N double bond. This ring is highly delocalized and therefore likely to be very stable. Outside the hexagons, the NN1 bond is slightly lengthened relative to the model N═N double bond, and the CN1 bond is slightly shortened relative to the model C−N single bond. This likely indicates that a degree of delocalization is likely stabilizing the chains connecting the hexagons as well. Electron delocalization in the $N_{12}C_4$ molecule stabilizes the structure, and this stability would enhance the potential usefulness of the molecule as a high-energy material.

Metal-Ion binding. Because the metal ions in this study are positively charged and the nitrogen atoms in $N_{12}C_4$ are polarized negative by carbon, and the metal-ion binding sites in this study all involve binding to nitrogen atoms. Three binding sites are shown in Figure 2: (a) the top site, at which the metal binds to a nitrogen pair from each hexagon, (b) the side site, at which the metal binds to four nitrogen atoms from the same hexagon, and (c) the end site, at which the metal ion binds to a nitrogen pair connecting the two hexagons. Other binding sites, including the body center of the $N_{12}C_4$ structure, were shown not to be local minima of the potential energy surface. The body center is not a minimum because the interior cavity is too small to fit the metal ions. Hence, the binding sites in this study all involve binding to the exterior of the structure. The results of the binding studies for the three sites are shown in Table 2.

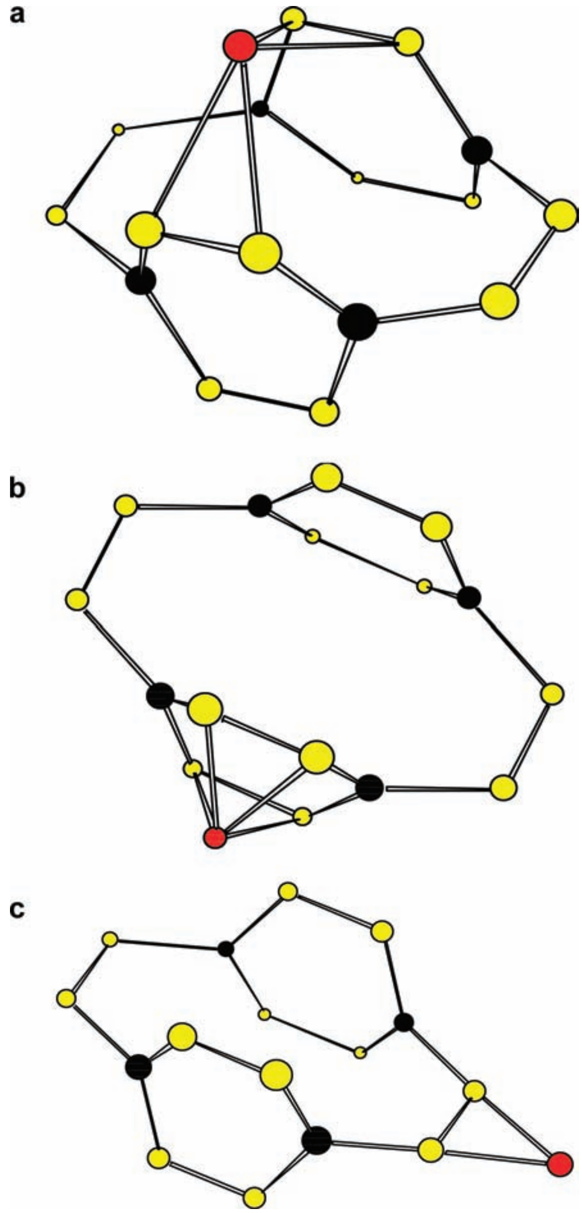

Figure 2. Metal-ion binding to $N_{12}C_4$: (a) TOP binding, (b) SIDE binding, and (c) END binding. Carbon atoms are shown in black, nitrogen atoms are shown in yellow, and the metal ion is shown in red.

Which binding site is preferred? Table 2 shows that the top binding site is preferred in all cases. This binding site has two advantages that allow for stronger cation binding. First, the site offers four negatively polarized nitrogen atoms, a rich site of negative charge suitable for metal-ion binding. By contrast, the end binding site only offers two nitrogen atoms for binding. Second, the advantage the top site has over the side binding site is that of geometric freedom. Whereas each site has four nitrogen atoms, the top site has more freedom to optimize the metal−nitrogen distance by rotating the hexagons to bring the nitrogen pairs closer to the metal ion. Conversely, the side

TABLE 2: Binding Energies (BE) of Metal Ions to the Various Binding Sites on the $N_{12}C_4$ Molecule, Calculated with PBE1PBE/cc-pVDZ and B3LYP/cc-pVDZ[a]

ion	binding site	BE(B3LYP)	BE(PBE1PBE)	BSSE	corrected BE
Li^+	top	36.1	34.3	3.7	30.6
	end	30.5	28.6	2.5	26.1
	side	6.3	5.1	2.9	2.2
Be^{2+}	top	230.0	226.0	4.4	221.6
	end	203.0	194.5	3.2	191.3
	side	165.2	163.3	5.1	158.2
Na^+	top	26.0	24.6	3.5	21.1
	end	21.0	19.8	2.3	17.5
	side	3.0	2.3	2.3	0.0
Mg^{2+}	top	126.8	123.0	4.0	119.0
	end	103.5	98.1	2.6	95.5
	side	68.7	65.3	3.5	61.8

[a] PBE1PBE counterpoise corrections to binding energies are included. Energies are shown in kcal/mol.

TABLE 3: Metal−Nitrogen Distances in the $MN_{12}C_4$ Molecules, Calculated with PBE1PBE/cc-pVDZ (Distances in Angstroms)[a]

ion	binding site	M−N distance
Li^+	top	2.22
	end	2.06
	side	2.52
Be^{2+}	top	1.74
	end	1.57
	side	1.77
Na^+	top	2.58
	end	2.43
	side	2.99
Mg^{2+}	top	2.17
	end	2.05
	side	2.31

[a] Note that all ion-bound molecules have C_{2v} point group symmetry and therefore have only one symmetry-independent M−N distance.

binding site consists of four nitrogen atoms from a rigid aromatic hexagon, which requires that either the nitrogen atoms remain farther from the metal ions or that the aromatic ring is bent to allow closer metal−nitrogen approach. The bending of the ring, however, leads to an energetic penalty and corresponding reduction in binding energy. Binding energy at the side site for the +1 cations is essentially nonexistent, resulting primarily as an artifact of BSSE. In fact, for sodium, the binding energy is entirely the result of BSSE, and the sodium ion does not bind to that site.

Metal−nitrogen distances are shown in Table 3. In all cases, the metal−nitrogen distances are shortest at the end binding site because this site offers complete geometric freedom to the metal ion because the ion can position itself anywhere along the long axis of the molecule without interacting with any atoms other than the nitrogen pair at the end site. The top site has somewhat longer metal−nitrogen distances because the freedom of the hexagons to optimize the binding site is not unlimited. For lithium, sodium, and magnesium, the metal−nitrogen distances are much longer for side binding than for the other two sites. This is because of the rigidity of the aromatic hexagon. Beryllium is exceptional in that the metal−nitrogen distances are about the same for the top and side binding sites. In beryllium's case, the combination of high electric charge and small ionic radius allows for a bending of the aromatic hexagon because the close approach of the small cation to the nitrogen provides sufficient binding energy to overcome the penalty for bending the ring. Nevertheless, even for beryllium, the side binding site is the least favorable.

Conclusions

The $N_{12}C_4$ molecule has structure properties that should render the molecule stable for high-energy applications. If additional stability can be conferred by binding a metal ion to the structure, then it is important to understand which binding sites are preferred energetically. Two factors have been shown to contribute to stability: (1) Maximizing the number of negatively polarized nitrogen atoms at the binding site, and (2) maximizing the geometric flexibility at the site to accommodate the metal ion. Structures such as $N_{12}C_4$ and their ion-bound counterparts may, if successfully synthesized, find broad application as high-energy sources.

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