

Stability of $N_{10}C_{10}H_{10}$ and $N_{12}C_{12}H_{12}$ Cages and the Effects of Endohedral Atoms and Ions

DeAna McAdory,[‡] Jacqueline Jones,[†] Ami Gilchrist,[†] Danielle Shields,[†]
Ramola Langham,[‡] Kasha Casey,[‡] and Douglas L. Strout^{*,‡}

*Departments of Biological Sciences and Physical Sciences, Alabama State University,
Montgomery, Alabama 36101*

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Abstract: Cages of carbon and nitrogen have been studied by theoretical calculations to determine the potential of these molecules as high-energy density materials. Following previous theoretical studies of high-energy $N_6C_6H_6$ and $N_8C_8H_8$ cages, a series of calculations on several isomers of the larger $N_{10}C_{10}H_{10}$ and $N_{12}C_{12}H_{12}$ is carried out to determine relative stability among a variety of three-coordinate cage isomers with four-membered, five-membered, and/or six-membered rings. Additionally, calculations are carried out on the same molecules with atoms or ions inside the cage. Calculations are carried out with the B3LYP and PBE1PBE density functional (DFT) methods, with MP2 and MP4 calculations carried out to evaluate the accuracy of the DFT results. Trends in stability with respect to cage geometry and arrangements of atoms are calculated and discussed. Stability effects caused by the endohedral atoms and ions are also 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.^{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 8–12 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 produced¹³ 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 survey²⁰ 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 study²¹ 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 study²² of larger nitrogen molecules N_{24} , N_{30} , and N_{36} showed significant deviations from the pentagon-favoring trend. A computational study²³ of the even larger cylindrical cage N_{72} has been carried out to elucidate the bonding properties of cylindrical nitrogen. Each of these molecule sizes has fullerene-like cages consisting solely of

* Corresponding author e-mail: dstROUT@alasu.edu.

[†] Department of Biological Sciences.

[‡] Department of Physical Sciences.

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^{24,25} 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 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, while it is possible to identify in relative terms which nitrogen cages are the most stable, it has been shown⁷ 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^{26,27} or phosphorus substitution.²⁸

A study²⁹ 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 study³⁰ of several isomers of $N_6C_6H_6$ showed that, for substitutions of carbon atoms 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. A similar study³¹ of numerous cage isomers of $N_8C_8H_8$ further illustrated the stabilizing effects of heteronuclear bonds. That study also showed that the N–N bonds in the $N_8C_8H_8$ cages can be strengthened by carbon atoms in the local environment.

In the current study, three isomers of $N_{10}C_{10}H_{10}$ and six isomers of $N_{12}C_{12}H_{12}$ are examined by theoretical calculations to determine their relative stability. The cages are also studied with endohedral atoms and ions. The noble gases helium, neon, and argon are studied. The ions Li^+ , Be^{2+} , Na^+ , Mg^{2+} , and Al^{3+} are also studied to determine their impact on the stability of the cage molecules. These molecules are also used to test the relative accuracy of density functional theory methods (specifically B3LYP and PBE1PBE). Trends of molecular stability are calculated and discussed.

Computational Methods

Geometries are optimized with two density functional theory (DFT) methods, the B3LYP method^{32,33} and the PBE1PBE method.³⁴ Optimizations of selected molecules are carried out with second-order perturbation theory³⁵ (MP2). Single energy points are calculated with fourth-order perturbation theory³⁵ (MP4(SDQ)). The basis set is the polarized valence double- ζ (cc-pVDZ) set of Dunning.³⁶ Atomic charges

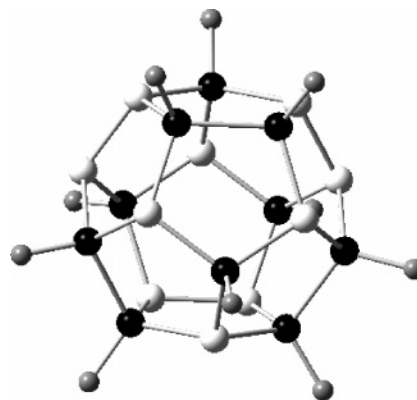


Figure 1. $N_{10}C_{10}H_{10}$ cage isomer A (C_s point group symmetry). Nitrogen atoms are shown in white, carbon atoms in black, and hydrogen atoms in gray.

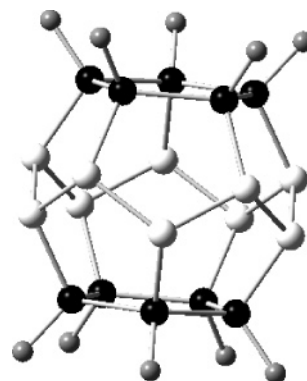


Figure 2. $N_{10}C_{10}H_{10}$ cage isomer B (D_{5d} point group symmetry). Nitrogen atoms are shown in white, carbon atoms in black, and hydrogen atoms in gray.

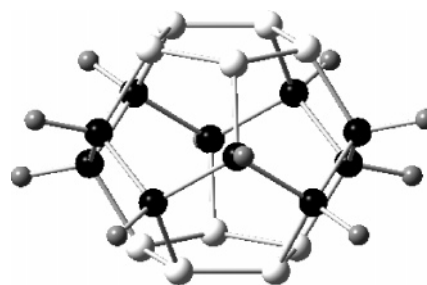


Figure 3. $N_{10}C_{10}H_{10}$ cage isomer C (D_{5d} point group symmetry). Nitrogen atoms are shown in white, carbon atoms in black, and hydrogen atoms in gray.

referred to in this work are Mulliken charges. Geometry optimizations with endohedral atoms or ions are full optimizations, with the cage permitted to relax structurally. The Gaussian03 computational chemistry software³⁷ (along with Windows counterpart Gaussian03W) has been used for all calculations in this study.

Results and Discussion

Three isomers of $N_{10}C_{10}H_{10}$ in this study are shown in Figures 1–3 and designated as isomers A–C. These are all based on carbon substitution on an N_{20} dodecahedron. Six isomers of $N_{12}C_{12}H_{12}$ are examined in this study, and they are shown in Figures 4–9. Each is named according to the polygons that make up the cage. The molecules in Figures 4–7 are

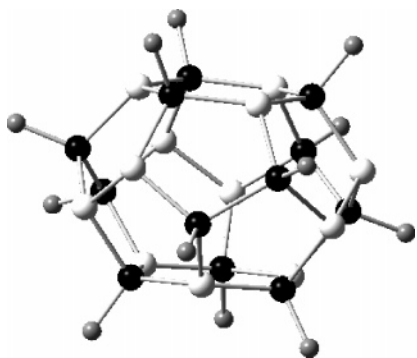


Figure 4. $N_{12}C_{12}H_{12}$ cage isomer 56A (D_{3d} point group symmetry). Nitrogen atoms are shown in white, carbon atoms in black, and hydrogen atoms in gray.

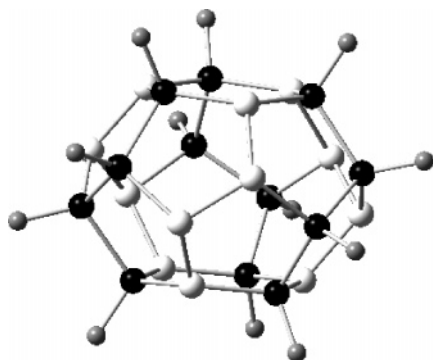


Figure 5. $N_{12}C_{12}H_{12}$ cage isomer 56B (D_{3d} point group symmetry). Nitrogen atoms are shown in white, carbon atoms in black, and hydrogen atoms in gray.

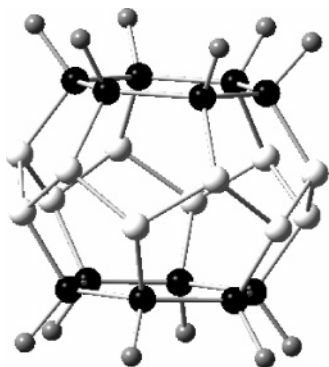


Figure 6. $N_{12}C_{12}H_{12}$ cage isomer 56C (D_{6d} point group symmetry). Nitrogen atoms are shown in white, carbon atoms in black, and hydrogen atoms in gray.

called 56A, 56B, 56C, and 56D because they are composed of five- and six-membered rings. Figures 8 and 9 show molecules 46 and 456, respectively, and they are so named because they incorporate four-membered rings. The relative energies of the $N_{10}C_{10}H_{10}$ isomers, calculated with B3LYP/cc-pVDZ and PBE1PBE/cc-pVDZ, are shown in Tables 1 and 2, respectively, and the energies of the $N_{12}C_{12}H_{12}$ cages are shown in Tables 3 and 4. Energies are shown for empty cages as well as for cages with endohedral atoms and ions. The following general trends are evident in the data.

Empty Cages. The two primary structural features that tend to destabilize these molecules are homonuclear bonds and four-membered rings. Homonuclear bonds are destabiliz-

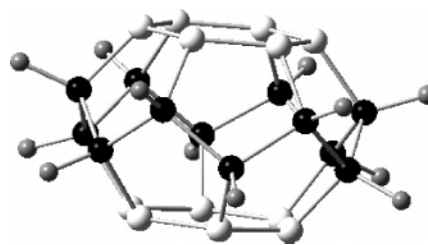


Figure 7. $N_{12}C_{12}H_{12}$ cage isomer 56D (D_{6d} point group symmetry). Nitrogen atoms are shown in white, carbon atoms in black, and hydrogen atoms in gray.

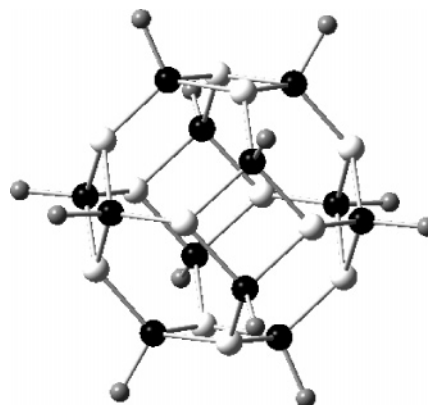


Figure 8. $N_{12}C_{12}H_{12}$ cage isomer 46 (T_h point group symmetry). Nitrogen atoms are shown in white, carbon atoms in black, and hydrogen atoms in gray.

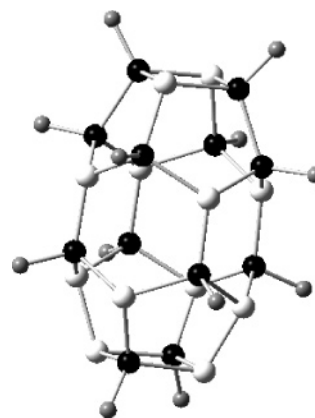


Figure 9. $N_{12}C_{12}H_{12}$ cage isomer 456 (C_{2v} point group symmetry). Nitrogen atoms are shown in white, carbon atoms in black, and hydrogen atoms in gray.

ing for these systems because a pair of C–N bonds has higher bond enthalpy than a C–C bond and an N–N bond. Therefore, increasing the number of heteronuclear bonds increases the stability of the molecules. This is evident for the $N_{10}C_{10}H_{10}$ cages, in which isomer A has only three pairs of homonuclear bonds, whereas isomers B and C have ten such pairs. As a result, isomer A is more stable (by over 100 kcal/mol) than isomers B and C. Also, four-membered rings are destabilizing because of ring strain from the 90° (approximately) angles. The two most stable $N_{12}C_{12}H_{12}$ cages, namely 56A and 456, are the most stable because they have small numbers of homonuclear bonds and four-membered rings. Isomer 56A has three pairs of homonuclear bonds (the minimum for the 56 architecture) and zero four-membered

Table 1. Relative Energies of N₁₀C₁₀H₁₀ Cage Isomers Calculated with the B3LYP/cc-pVDZ Method^a

interior	isomer A	isomer B	isomer C
empty	0.0	+119.2	+129.0
He	0.0	+110.9	+121.0
Ne	0.0	+96.2	+107.5
Ar	0.0	+67.4	+78.9
Li ⁺	0.0	+121.7	+130.3
Be ²⁺	0.0	+152.7	+156.7
Na ⁺	0.0	+105.2	+116.1
Mg ²⁺	0.0	+121.4	+130.5
Al ³⁺	0.0	+152.0	+158.4

^a Results are shown for empty cages and cages with endohedral atoms and ions. Energies are in kcal/mol.

Table 2. Relative Energies of N₁₀C₁₀H₁₀ Cage Isomers Calculated with the PBE1PBE/cc-pVDZ Method^a

interior	isomer A	isomer B	isomer C
empty	0.0	+124.3	+134.1
He	0.0	+116.5	+126.6
Ne	0.0	+102.2	+113.6
Ar	0.0	+74.9	+86.7
Li ⁺	0.0	+127.3	+136.1
Be ²⁺	0.0	+159.0	+163.0
Na ⁺	0.0	+111.3	+122.3
Mg ²⁺	0.0	+127.6	+137.0
Al ³⁺	0.0	+158.3	+165.2

^a Results are shown for empty cages and cages with endohedral atoms and ions. Energies are in kcal/mol.

Table 3. Relative Energies of N₁₂C₁₂H₁₂ Cage Isomers Calculated with the B3LYP/cc-pVDZ Method^a

interior	56A	56B	56C	56D	46	456
empty	0.0	+107.3	+170.6	+217.4	+76.9	+5.2
He	0.0	+101.7	+154.9	+208.3	+64.2	+28.9
Ne	0.0	+93.7	+136.5	+199.1	+50.2	+75.3
Ar	0.0	+74.4	+97.0	+173.2	+25.5	+146.1
Li ⁺	0.0	+108.7	+192.0	+219.2	+72.2	+23.0
Be ²⁺	0.0	+93.1	+301.3	+272.6	+118.9	+33.6
Na ⁺	0.0	+99.9	+159.8	+205.7	+50.9	+64.5
Mg ²⁺	0.0	+109.8	+208.2	+223.7	+59.3	+51.5
Al ³⁺	0.0	+102.1	+308.3	+272.9	+87.7	+61.5

^a Results are shown for empty cages and cages with endohedral atoms and ions. Energies are in kcal/mol.

rings, whereas isomer 456 has two pairs of homonuclear bonds and two four-membered rings. The other isomers in this study have either at least nine pairs of homonuclear bonds (isomers 56B, 56C, and 56D) or six four-membered rings (isomer 46). Those isomers are all much higher in energy than isomers 56A and 456.

Geometric Effects and Noble Gases. In terms of structure, all three isomers of N₁₀C₁₀H₁₀ are based on the dodecahedron and have very similar shape. However, Tables 1 and 2 show a systematic variation in energy with the size of the noble gas atoms. With increasing atom size, isomers B and C become more stable. The answer lies in a more detailed analysis of structure. For isomers B and C, the atoms are on average 2.09 Å from the center (PBE1PBE/cc-pVDZ). Isomer A is slightly smaller, with an average distance of 2.06 Å from the center. A few hundredths of an angstrom

Table 4. Relative Energies of N₁₂C₁₂H₁₂ Cage Isomers Calculated with the PBE1PBE/cc-pVDZ Method^a

interior	56A	56B	56C	56D	46	456
empty	0.0	+111.4	+178.6	+197.3	+78.8	+4.9
He	0.0	+106.1	+162.1	+217.2	+65.4	+27.4
Ne	0.0	+102.0	+143.4	+209.7	+51.5	+76.4
Ar	0.0	+80.6	+102.9	+188.1	+27.2	+153.2
Li ⁺	0.0	+112.8	+200.4	+228.3	+73.4	+22.6
Be ²⁺	0.0	+96.3	+309.7	+281.1	+119.1	+35.9
Na ⁺	0.0	+104.6	+166.6	+216.4	+51.5	+66.9
Mg ²⁺	0.0	+114.7	+215.3	+234.3	+59.2	+54.2
Al ³⁺	0.0	+108.0	+312.9	+282.3	+85.0	+63.7

^a Results are shown for empty cages and cages with endohedral atoms and ions. Energies are in kcal/mol.

may not seem significant, but in terms of crowding a noble gas atom (especially an argon atom with a radius of 1.74 Å), the energetic effect is substantial.

Regarding the isomers of N₁₂C₁₂H₁₂, the 56 isomers all have more or less the same structure. Isomer 46 is unique in that it is the most spherical of all isomers in this study. The spherical interior of isomer 46 is the best suited to enclose the progression of increasingly large noble gases (He, Ne, Ar). Tables 3 and 4 show that the relative energy of isomer 46 decreases rapidly as endohedral noble gas size is increased. Conversely, isomer 456 has a narrow, crowded center (16 atoms close to the molecule's center). Therefore, this molecule is severely strained by the inclusion of endohedral noble gases. Tables 3 and 4 show that the energy of isomer 456 increases greatly with increasing noble gas size.

Isomeric Structure and Endohedral Cations. The data in Tables 3 and 4 also show interesting variations among the N₁₂C₁₂H₁₂ cages regarding the endohedral metal cations. The four isomers of type 56 have very similar geometric structure, but they vary in the number of nitrogen atoms in the axial hexagons, as opposed to the equatorial belt between the pentagons. Isomers 56A and 56B have three nitrogens in each hexagon (six total), whereas 56C has all 12 nitrogens in the equatorial belt, and isomer 56D has all 12 nitrogens in the axial hexagons. The arrangement of the hexagons is important because the C–N bonds in the cage structures are polar bonds. The nitrogen atoms take on a partial negative charge because of their greater electronegativity relative to carbon.

Because of the oblate structure of the 56 framework, the atoms in the axial hexagons are closer to the molecule's center than the atoms in the equatorial belt. This explains why isomer 56D becomes more stable than 56C in the presence of highly charged endohedral cations. The cations, especially the highly charged Be²⁺ and Al³⁺, experience a highly negatively charged environment in isomer 56D because of their proximity to the 12 nitrogens. The interaction between metal cations and negatively charged nitrogen stabilizes the entire structure. Tables 3 and 4 show that, for Be²⁺@N₁₂C₁₂H₁₂ and Al³⁺@N₁₂C₁₂H₁₂, isomer 56D is lower in energy than isomer 56C.

56A and 56B are stabilized relative to 56C and 56D in the presence of endohedral cations because the polarity of the C–N bonds in the hexagons causes the partial negative

Table 5. Comparison of B3LYP/cc-pVDZ and PBE1PBE/cc-pVDZ Results for $N_{12}C_{12}H_{12}$ Cages^a

molecule/interior	B3LYP	PBE1PBE	MP2	MP4//MP2
456/empty	+5.2	+4.9	−2.9	−0.7
456/He	+28.9	+27.4	+21.0	+24.0
456/Ne	+75.3	+76.4	+70.6	+73.8
456/Ar	+146.1	+153.2	+148.8	+155.7
56B/empty	+107.3	+111.4	+117.1	+116.4
56B/He	+101.7	+106.1	+110.5	+110.6
56B/Ne	+93.7	+102.0	+102.4	+103.3
56B/Ar	+74.4	+80.6	+81.3	+84.2
46/empty	+76.9	+78.8	+85.3	+82.0
56C/empty	+170.6	+178.6	+183.7	+182.6
56D/empty	+217.4	+197.4	+235.1	+233.3

^a Energies are in kcal/mol, relative to the energy of isomer 56A. For each molecule, the DFT result closest to MP4 is shown in bold.

charge on the axial nitrogens to be greater in isomers 56A and 56B. At the PBE1PBE/cc-pVDZ level of theory, for example, the axial nitrogens of isomers 56A and 56B have charges of −0.36 and −0.28 electrons, respectively, as opposed to −0.14 electrons in isomer 56D (56C has no axial hexagon nitrogens). The larger nitrogen charges stabilize the cations in isomers 56A and 56B and lower their energies relative to 56C and 56D.

For the $N_{10}C_{10}H_{10}$ cages, the effects of oblate structure and axial vs equatorial nitrogens are a nonissue, because, in the dodecahedron, all 20 cage positions are about the same distance from the center. Therefore, placement of the nitrogen atoms is irrelevant to the interaction between the cage and the cations. The data in Tables 1 and 2 bear this out. For the empty cages, isomer B is more stable than isomer C by 10 kcal/mol. For the endohedral cations, isomer B is more stable than isomer C by 4–12 kcal/mol in all cases, so the isomer energy reversals and larger swings in energy shown for $N_{12}C_{12}H_{12}$ (especially isomers 56C and 56D) do not occur for $N_{10}C_{10}H_{10}$.

Relative Accuracy of the DFT Methods. For selected cages and interiors, MP2/cc-pVDZ geometries have been optimized, and MP4(SDQ)/cc-pVDZ energies have been calculated at the MP2 geometries. These results are used as a benchmark for determining the relative accuracy of the B3LYP and PBE1PBE methods. B3LYP is a long-standing functional with a long track record, and the PBE1PBE functional is representative of a more recent approach that has been shown^{38–41} to give good results for molecules and solids. The comparison in this study is intended to test the two functionals for large molecules. The results are shown in Table 5. In nine of the 11 trials, the PBE1PBE outperformed B3LYP. In those nine trials, the PBE1PBE method recovered, on average, 51% of the energy difference between B3LYP and MP4(SDQ). In the four trials involving isomer 56B, the isomer most structurally similar to reference molecule 56A, PBE1PBE, was more successful across the board, recovering an average of 61% of the energy difference between B3LYP and MP4(SDQ).

Energy Release upon Decomposition. Table 6 shows the results of energy calculations on the reaction $X@N_{12}C_{12}H_{12} \rightarrow 6N_2 + 2C_6H_6 + X$, where X is the endohedral atom or

Table 6. Energy Release Properties of $N_{12}C_{12}H_{12}$ Isomer 56A, Calculated with the PBE1PBE Method and the Cc-pVDZ Basis Set^a

X	energy (kcal/mol)	energy (kcal/g)
none	157	0.49
He	194	0.59
Ne	250	0.73
Ar	465	1.28
Li ⁺	142	0.43
Be ²⁺	131	0.39
Na ⁺	225	0.65
Mg ²⁺	51	0.16
Al ³⁺	333	0.95

^a The reaction $X@N_{12}C_{12}H_{12} \rightarrow 6N_2 + 2C_6H_6 + X$ is used to model the decomposition. X = endohedral atom or ion.

ion. Isomer 56A is chosen for study because it is the most stable isomer of $N_{12}C_{12}H_{12}$. Since 56A has very few of the relatively weak N–N bonds and none of the sterically strained four-membered rings, it is the best candidate for a kinetically stable high-energy material. The data in Table 6, calculated at the PBE1PBE/cc-pVDZ level of theory, show the energy properties of isomer 56A of $N_{12}C_{12}H_{12}$ and the influence of the endohedral atoms/ions on the energy properties. In general, the noble gases increase the energy release of the cage because steric repulsions between the noble gases and the cage raise the energy of the cage, an effect that increases with increasing size of the noble gas atom. The first-row ions decrease the energy release of the cage, because the cage is stabilized by ion-dipole interactions between the ion and the cage. The second-row ions are most likely causing both steric interactions (destabilizing) and ion-dipole interactions (stabilizing), and therefore the influence of second-row atoms on the energy release properties is more erratic.

Conclusions

The following conclusions arise from this study: (1) Four-membered rings and homonuclear bonds are the primary destabilizing factors for $N_{10}C_{10}H_{10}$ and $N_{12}C_{12}H_{12}$ cages. (2) The ability of the cages to accommodate noble gases depends primarily on the size and shape of the interior cavity of each cage but less dependent on the precise placement of individual atoms. (3) The ability of the cages to accommodate cations is very dependent on the precise placement of atoms on the framework, especially regarding the proximity of nitrogen atoms to the molecule's center. (4) The PBE1PBE density functional method consistently outperforms B3LYP for these systems.

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