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Theoretical Study on "Multilayer" Nitrogen Cages

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The relative stabilities of nonisomers are investigated. Twenty-two species of nitrogen cage molecules N_{2n} (N_6 (D_{3h}), N_8 (O_h), N_{10} (D_{5h}), N_{12} (D_{6h}), N_{12} (D_{3d}), N_{16} (D_{4d}), N_{18} (D_{3h}), N_{20} (I_h), N_{24} (D_{3d}), N_{24} (D_{4h}), N_{24} (D_{6d}), N_{30} (D_{3h}), N_{30} (D_{5h}), N_{32} (D_{4d}), N_{36} (D_{3d}), N_{40} (D_{4h}), N_{42} (D_{3h}), N_{48} (D_{4d}), N_{48} (D_{3d}), N_{54} (D_{3h}), N_{56} (D_{4h}), and N_{60} (D_{3d})), which are divided into four sets, have been studied in detail. The geometries and varieties of energies are examined extensively, and NBO analysis and AIM analysis are applied to investigate the bonding properties of the cage molecules. The introducing of the concept of "layer" can well assist in explaining why one nonisomer molecule is more stable than another one. The results show that the lengths of bonds, on both sides of which are five-membered rings (referred to as pentagons), are the shortest and the orbital energies are the lowest. The nonlocalized electron numbers of orbitals, on at least one side of which is a triangle, are the greatest. Pentagons play a major role in the stability of a cage molecule, and the three-membered rings (referred to as triangles) play the second one. The layers in nitrogen cage molecules also contribute to the relative stabilities.

1. Introduction

In the past 20 years, pure nitrogen clusters have been extensively studied as possible candidates for high energy density materials (HEDMs),[1−21] due to the dissociation of polynitrogen molecule into N_2 molecules with the release of a large amount of energy, which can be used as propellants and explosives.[1] However, to be good candidates for HEDMs, polynitrogen molecules need to possess the resistance to dissociation to some extent. So, the relative stabilities of polynitrogen molecules have become the focus of recent experimental and theoretical research. There have been many theoretical studies at various computational levels on the clusters containing an even number of nitrogen atoms, such as N_4,[1,2] N_6,[1−3] N_8,[1−9] N_{10},[1,9−14] N_{12},[1,9,13,15,16] N_{14},[9,17,18] N_{16},[9] N_{18},[19] N_{20},[9,11,20] N_{24},[9,21] N_{30},[11,21] N_{36},[21] and N_{60}.[11] These theoretical investigations show that many N_{2n} ($n \geq 2$) clusters have much higher energies than those of n N_2 molecules. All of these clusters can be regard as potential HEDMs, even though most, if not all, of them still await experimental confirmation.

The stabilities of N_{2n} molecules have also been extensively studied in a computational survey[1,15,21] of various structural forms with up to 36 atoms. Cyclic, acyclic, and cage isomers have been studied to examine the bondings and energies over a wide range of molecules. The computational studies of cage isomers of N_{12},[15] N_{24}, N_{30}, and N_{36}[21] examined specific structural features that led to the most stable molecules among 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. However, the method recommended by refs 15 and 21 for estimating relative stabilities of molecules is strictly confined in isomers. That is, if the molecules are not isomers, the relative stabilities cannot be evaluated using this method. For example, the question of which is more stable of the molecules N_{12} (D_{3d}) and N_{16} (D_{4d}) remains difficult to be answered up to the present. Chen et al.[9] tried to estimate the relative stabilities of the molecules N_8, N_{10}, N_{12}, N_{14}, N_{16}, N_{20}, and N_{24} by introducing the concept of "average bonding energy". But, the most important precondition of this method is that the bond type in the molecules must be the same. More recently, we have tried to develop a simple method for estimating the relative stabilities of chemical substances with the same empirical formula and obtained some useful results (the details will be introduced in section 2). All N_{2n} molecules can be considered as chemical substances with the same empirical formula, so, the relative stabilities of N_{2n} molecules can be estimated using their group energies (GEs) or group heats of formation (GHOFs) because this method does not require any precondition of molecule structure.

2. Methods

Twenty-two species of N_{2n} molecules (N_6 (D_{3h}), N_8 (O_h), N_{10} (D_{5h}), N_{12} (D_{6h}), N_{12} (D_{3d}), N_{16} (D_{4d}), N_{18} (D_{3h}), N_{20} (I_h), N_{24} (D_{3d}), N_{24} (D_{4h}), N_{24} (D_{6d}), N_{30} (D_{3h}), N_{30} (D_{5h}), N_{32} (D_{4d}), N_{36} (D_{3d}), N_{40} (D_{4h}), N_{42} (D_{3h}), N_{48} (D_{4d}), N_{48} (D_{3d}), N_{54} (D_{3h}), N_{56} (D_{4h}), and N_{60} (D_{3d})) are studied. The geometric structures and total energies of N_6 (D_{3h}), N_8 (O_h), N_{10} (D_{5h}), N_{12} (D_{6h}), N_{12} (D_{3d}), N_{16} (D_{4d}), N_{18} (D_{3h}), N_{20} (I_h), N_{24} (D_{6d}), N_{24} (D_{4h}), N_{24} (D_{3d}), N_{30} (D_{3h}), N_{30} (D_{5h}), and N_{36} (D_{3d}) have been reported.[1−21] The optimization and energy calculation of unreported molecules N_{32} (D_{4d}), N_{40} (D_{4h}), N_{42} (D_{3h}), N_{48} (D_{4d}), N_{48} (D_{3d}), N_{54} (D_{3h}), N_{56} (D_{4h}), and N_{60} (D_{3d}) are carried out. For the convenience of study, the concept of "layer" is introduced to assist in estimating the relative stabilities of nonisomer molecules. The term "layer" can be defined as follows: (1) All atoms belonging to the same layer are coplanar. (2) All layers in one molecule are parallel to each other. (3) All layers in one molecule are perpendicular to its C_n principal axis.

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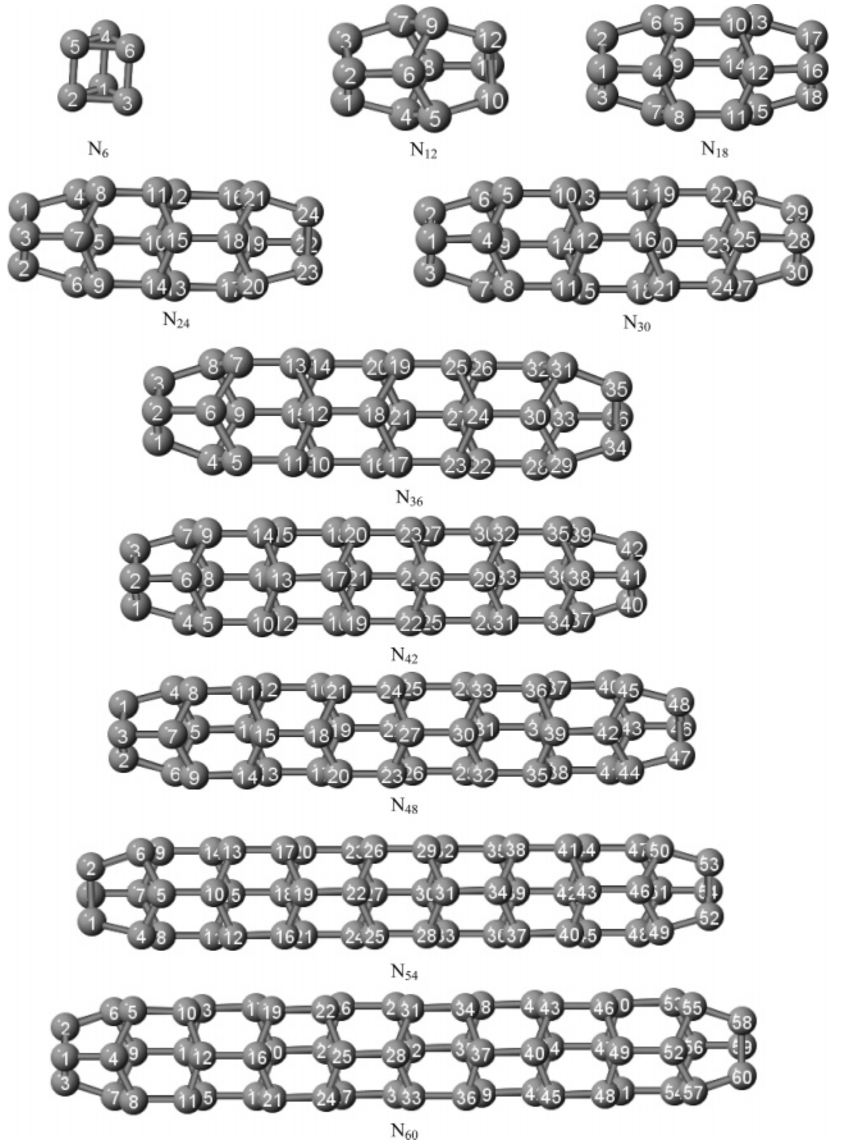

Figure 1. The optimized structures of the 10 molecules in the **3M** set.

According to this definition, all of the 22 species N_{2n} were divided into four sets by the different number of atoms in the same plane or layer. The four sets are denoted by ***n*M** (n = 3−6) sets, respectively.

2.1. 3M Set. The main characteristic of this set is that each layer in the molecules contains three atoms. There are 10 molecules in this set: N_6 (D_{3h}), N_{12} (D_{3d}), N_{18} (D_{3h}), N_{24} (D_{3d}), N_{30} (D_{3h}), N_{36} (D_{3d}), N_{42} (D_{3h}), N_{48} (D_{3d}) N_{54} (D_{3h}), and N_{60} (D_{3d}). For the molecules in this set, N_6 (D_{3h}) is chosen as the mother molecule. The rest can be regarded as derivatives from the mother molecule. The molecule N_{12} (D_{3d}) can be considered as one W-shape (chair-form) six-membered ring (referred to as a hexagon) being inserted into the mother molecule. The atoms in the ring link to the atoms in the top layer and link to the atoms in the bottom layer of the mother molecule alternatively. The three atoms in the hexagon linking to the top layer atoms in the mother molecule form one plane (one layer), and the remaining three atoms in the hexagon linking to the bottom layer atoms form another plane (another layer). Analogously, the molecule N_{18} (D_{3h}) can be considered as two hexagons with a W-shape being inserted into the mother molecule. The molecules N_{24} (D_{3d}), N_{30} (D_{3h}), N_{36} (D_{3d}), N_{42} (D_{3h}), N_{48} (D_{3d}), N_{54} (D_{3h}), and N_{60} (D_{3d}) can be formed in the same manner. Two new layers are added when one W-shape hexagon is inserted into the mother molecule. Thus, the layer numbers of the molecules N_6 (D_{3h}), N_{12} (D_{3d}), N_{18} (D_{3h}), N_{24} (D_{3d}), N_{30} (D_{3h}), N_{36} (D_{3d}), N_{42} (D_{3h}), N_{48} (D_{3d}), N_{54} (D_{3h}), and N_{60} (D_{3d}) are 2, 4, 6, 8, 10, 12, 14, 16, 18, and 20, respectively. All of the molecules are "multilayer" nitrogen cages.

2.2. 4M Set. The main characteristic of this set is that each layer in the molecules contains four atoms. There are 7 molecules in this set: N_8 (O_h), N_{16} (D_{4d}), N_{24} (D_{4h}), N_{32} (D_{4d}), N_{40} (D_{4h}), N_{48} (D_{4d}), and N_{56} (D_{4h}). For the molecules in this set, N_8 (O_h) is chosen as the mother molecule. The molecule N_{16} (D_{4d}) can be considered as one W-shape eight-membered ring being inserted into the mother molecule. The molecules N_{24} (D_{4h}), N_{32} (D_{4d}), N_{40} (D_{4h}), N_{48} (D_{4d}), and N_{56} (D_{4h}) can be constructed in the same way. The layer numbers of the molecules N_8 (O_h), N_{16} (D_{4d}), N_{24} (D_{4h}), N_{32} (D_{4d}), N_{40} (D_{4h}), N_{48} (D_{4d}), and N_{56} (D_{4h}) are 2, 4, 6, 8, 10, 12, and 14, respectively. They are "multilayer" molecules, too.

2.3. 5M Set. The main characteristic of this set is that each layer in the molecules contains five atoms. There are 3 molecules in this set: N_{10} (D_{5h}), N_{20} (I_h), and N_{30} (D_{5d}). For the molecules in this set, N_{10} (D_{5h}) is chosen as the mother molecule. The molecule N_{20} (I_h) can be considered as one ten-

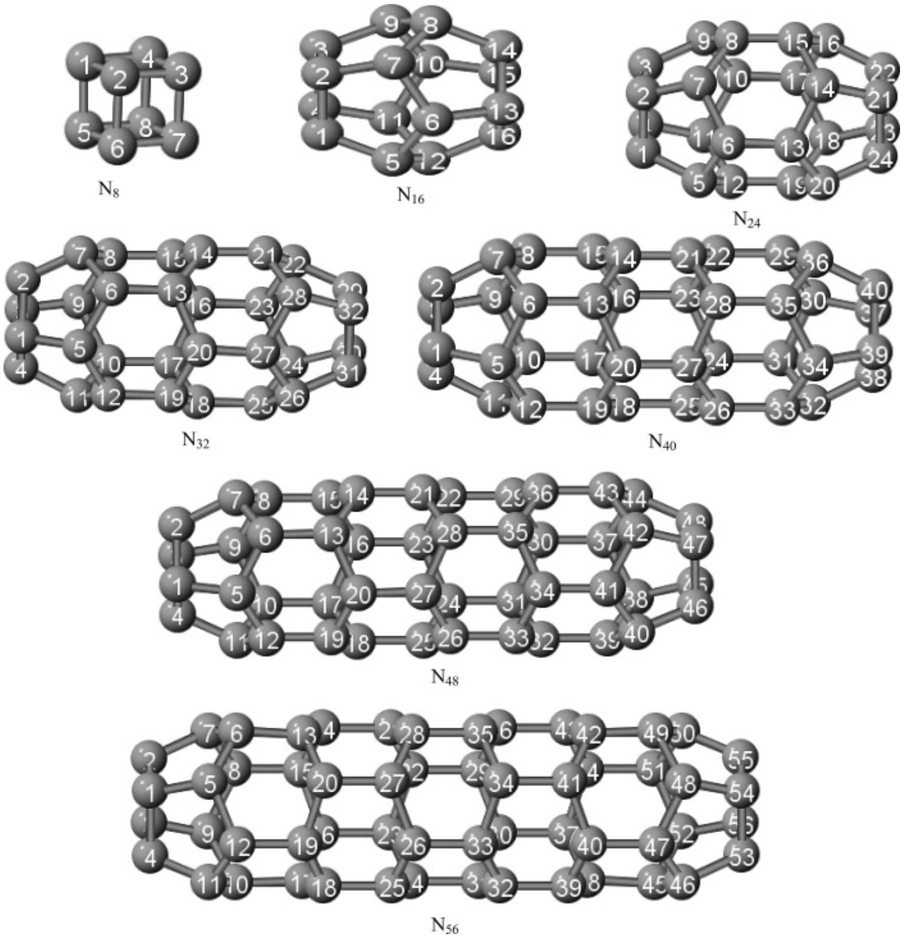

Figure 2. The optimized structures of the 7 molecules in the **4M** set.

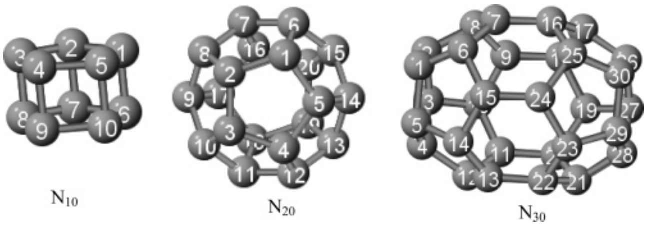

Figure 3. The optimized structures of the 3 molecules in the **5M** set.

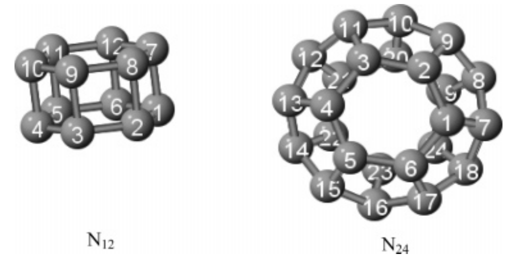

Figure 4. The optimized structures of the 2 molecules in the **6M** set.

TABLE 1: Selected Bond Lengths (Å) of the 10 Molecules in the 3M Set

bond	N_6	N_{12}	N_{18}	N_{24}	N_{30}	N_{36}	N_{42}	N_{48}	N_{54}	N_{60}
$R_{1,2}$	1.481	1.532	1.526	1.528	1.527	1.529	1.529	1.528	1.528	1.529
$R_{1,4}$	1.524	1.420	1.432	1.428	1.429	1.428	1.428	1.428	1.428	1.428
$R_{4,5}$	1.481	1.494	1.477	1.484	1.482	1.483	1.482	1.483	1.482	1.484
$R_{5,10}$		1.420	1.479	1.485	1.483	1.483	1.484	1.483	1.484	1.484
$R_{10,12}$		1.532	1.477	1.456	1.460	1.459	1.458	1.459	1.459	1.459
$R_{12,16}$			1.432	1.485	1.491	1.492	1.492	1.492	1.492	1.492

membered ring with a W-shape being inserted into the mother molecule. Molecule N_{30} (D_{5d}) can be constructed by inserting two ten-membered rings with a W-shape into the mother molecule. The layer numbers of the molecules N_{10} (D_{5h}), N_{20} (I_h), and N_{30} (D_{5d}) are 2, 4, and 6, respectively.

2.4. 6M Set. The main characteristic of this set is that each layer in the molecules contains six atoms. There are 2 molecules in this set: N_{12} (D_{6h}) and N_{24} (D_{6d}). In this set, N_{12} (D_{6h}) is chosen as the mother molecule. The molecule N_{24} (D_{6d}) can be considered as one twelve-membered ring with a W-shape being inserted into the mother molecule. The layer numbers of the molecules N_{12} (D_{6h}) and N_{24} (D_{6d}) are 2 and 4, respectively.

We have carried out theoretical studies of the N_{2n} clusters using Gaussian 98 A.11 packages.[23] Density functional theory (DFT) has been applied to optimize the structures of the 22 species' N_{2n} cages at basis set CC-PVDZ. The basis set is the correlation-consistent basis set of Dunning, specifically the polarized valence double-ζ (CC-PVDZ). The convergence criterion is 10^{-8}. The optimized structures of the 22 species at B3LYP/CC-PVDZ are shown in Figures 1−4. The selected geometry parameters are listed in Tables 1−4.

The topological properties of bonds in a molecule have a significant influence on the thermodynamic stability of the molecule. So, natural bond orbital (NBO) analysis[24] and atoms in molecules (AIM) analysis[25] are carried to study the bonding properties of the N_{2n} clusters. The selected orbital energies from the NBO analysis are listed in Tables 5−8. The Laplacians of ρ ($\nabla^2\rho$) of bond critical points (BCPs) from AIM analysis are listed in Tables 9−12.

TABLE 2: Selected Bond Lengths (Å) of the 7 Molecules in the 4M Set

bond	N_8	N_{16}	N_{24}	N_{32}	N_{40}	N_{48}	N_{56}
$R_{1,2}$	1.522	1.547	1.569	1.574	1.574	1.571	1.575
$R_{1,5}$	1.523	1.437	1.427	1.419	1.420	1.422	1.420
$R_{5,6}$	1.523	1.495	1.477	1.489	1.488	1.488	1.488
$R_{6,13}$		1.437	1.468	1.470	1.468	1.469	1.468
$R_{13,14}$		1.547	1.477	1.434	1.441	1.439	1.441
$R_{14,21}$							

TABLE 3: Selected Bond Lengths (Å) of the 4 Molecules in the 5M Set

bond	N_{10}	N_{20}	N_{30}	bond	N_{10}	N_{20}	N_{30}
$R_{1,2}$	1.500	1.493	1.559	$R_{7,16}$		1.493	1.476
$R_{1,6}$	1.520	1.494	1.441	$R_{16,17}$		1.493	1.488
$R_{6,7}$	1.500	1.493	1.488	$R_{17,26}$			1.441

TABLE 4: Selected Bond Lengths (Å) of the 3 Molecules in the 6M Set

bond	N_{12}	N_{24}	bond	N_{12}	N_{24}
$R_{1,2}$	1.507	1.475	$R_{8,19}$		1.528
$R_{1,7}$	1.513	1.530	$R_{19,20}$		1.474
$R_{7,8}$	1.507	1.471			

The relative stability of a molecule is correlative with its electron structure. The concept of hyperconjugation arose within the framework of qualitative valence bond (VB) theory as a stabilizing and charge delocalization mechanism for carbocations and intermediates in electrophilic aromatic substitution which could be expressed in terms of bond no-bond canonical structure. Later the concept was extended to explain the supposed extra stabilization of carbanions by electron-withdrawing substitutents attached to adjacent carbon atoms (negative or anionic hyperconjugation).[26] This means that delocalization of charge on one atom can transfer to another bond or group. Theoretical evidence has been adduced to support the view that the charge delocalization is not negligible. Raban and co-workers[27] had used hyperconjugation to rationalize effects on nitrogen inversion barriers. In cases where an electron-withdrawing group (capable of bearing a negative charge) was located to a nitrogen atom, a substantial decrease in the nitrogen inversion barrier was observed. Hyperconjugation has been associated mainly with the effects in ionic species. So, Kost and Raban[28] expanded it to neutral molecules. The hyperconjugation interaction in a molecule can lead to a number of geometrical consequences. (1) It is a factor of strengthening an acceptor's bond which translates into a shortening of the acceptor's bond length, and inversely, it is a factor weakening a donor's bond which translates into a lengthening of the donor's bond length. (2) Hyperconjugation interaction plays an important role in molecule stability. The existence of such interaction renders a molecule more stable than when it does not occur. Hyperconjugation can be measured by nonlocalization degrees (nonlocalization degree is defined as 2.0 minus electron occupancies in one bonding orbital). Parts of nonlocalized electron numbers of orbitals are list in Tables 13 and 14.

The relative stabilities of molecules are usually estimated by the heats of formation (ΔH_f) of molecules. The well-known methods for calculating ΔH_f are the recently proposed G3 model of theory[29] and G3MP2 of theory.[30] However, it is difficult to obtain the ΔH_f of large molecules (for example, the number of heavy atoms is more than 15) using the G3 or G3MP2 model because both of them demand a large amount of computer resources with the increasing of basis functions. The ΔH_f of large molecules at B3LYP/CC-PVDZ can be calculated using the following formulas.

For the reaction reactants → product, the heats of formation at 298 K (ΔH_{f298}) can be calculated by

$$\Delta H_{f298} = H_{rxn} + \Delta H_{exp,0} + \Delta H_m - \Delta H_{atom} \tag{1}$$

where $H_{rxn} = E_{total\ (product,0K)} - \sum E_{atom,reactants}$; $H_{exp,0} = \sum H_{atom(exp,reactants)}$, thereof $H_{atom(exp,reactants)}$ can be obtained from ref 22; $\Delta H_m = H_{product} - E_{total(product,0K)}$; $\Delta \mathrm{H}_{atom} = \sum H_{cor(atom,exp)}$, thereof $H_{cor(atom,exp)}$ can be obtained from ref 22.

Equation 1 is applied to calculate the ΔH_f of a compound in G3 theory[29] and G3MP2 theory,[30] where total energy of the product and total energy of each atom of the reactants are referred as "G3 (0 K)" or "G3MP2 (0 K)". "G3 (0 K)" and "G3MP2 (0 K)" are modified by a series of corrections from additional calculations, including a correction for diffuse functions,

$$\Delta E(+) = E[\mathrm{MP4/6\text{-}31{+}G(d)}] - E[\mathrm{MP4/6\text{-}31G(d)}] \tag{2}$$

and a correction for higher polarization functions on nonhydrogen atoms and p-functions on hydrogen atom,[29,30]

$$\Delta E(\mathrm{2df,p}) = E[\mathrm{MP4/6\text{-}31G(2df,p)}] - E[\mathrm{MP4/6\text{-}31G(d)}] \tag{3}$$

etc.

In our work, we can only obtain the total energy at the level B3LYP/CC-PVDZ. Similarly to G3 theory and G3MP2 theory, the total energy at the level B3LYP/CC-PVDZ is modified by a correction for diffuse functions,

$$\Delta E(+) = E[\mathrm{B3LYP/6\text{-}31{+}G(d)}] - E[\mathrm{B3LYP/6\text{-}31G(d)}] \tag{4}$$

and a correction for higher polarization functions on nonhydrogen atoms and p-functions on hydrogen atom,

$$\Delta \mathrm{E(2df,p)} = E[\mathrm{B3LYP/6\text{-}31G(2df,p)}] - E[\mathrm{B3LYP/6\text{-}31G(d)}] \tag{5}$$

Comparing with the basis set of 6-31G(d), the CC-PVDZ basis set has had redundant functions removed. So, the total energy which has been corrected is

$$E_0(\mathrm{DFT}) = E[\mathrm{B3LYP/CC\text{-}PVDZ}] - \Delta E(+) - \Delta E(\mathrm{2df,p}) \tag{6}$$

where E_0(DFT) is the energy of each atom of the reactants that eq 1 requires. Note that for H (hydrogen) − O (oxygen) atoms, $\Delta E(+)$ will be removed from E_0(DFT); for fluorine atom, ΔE(2df,p) will be removed from E_0(DFT).

Now, the total energy and the enthalpy of the product can be obtained from quantum chemistry calculation directly. The $\Delta H_{exp,0}$ and $\Delta \mathrm{H}_{atom}$ can be obtained from correlative webs or references.[22]

The GE of N_{2n} can be calculated by

$$\mathrm{GE} = \frac{1}{2n} E_{N_{2n}} \tag{7}$$

where $E_{N_{2n}}$ is the total energy of molecular N_{2n}.

The ΔH_f of a molecule at the level B3LYP/CC-PVDZ can be calculated by eq 1 via eq 6.

$$\mathrm{GHOF} = \Delta H_{f298}/2n \tag{8}$$

TABLE 5: Selected Orbital Energies (au) of the 10 Molecules in the 3M Set

bond	N_6	N_{12}	N_{18}	N_{24}	N_{30}	N_{36}	N_{42}	N_{48}	N_{54}	N_{60}
$R_{1,2}$	−0.716	−0.698	−0.709	−0.707	−0.709	−0.706	−0.707	−0.707	−0.708	−0.708
$R_{1,4}$	−0.748	−0.903	−0.890	−0.897	−0.895	−0.898	−0.897	−0.897	−0.898	−0.898
$R_{4,5}$	−0.715	−0.820	−0.848	−0.845	−0.847	−0.845	−0.847	−0.846	−0.847	−0.846
$R_{5,10}$		−0.903	−0.868	−0.865	−0.867	−0.867	−0.867	−0.867	−0.867	−0.866
$R_{10,12}$		−0.698	−0.848	−0.883	−0.880	−0.882	−0.883	−0.882	−0.883	−0.883
$R_{12,16}$			−0.890	−0.865	−0.862	−0.862	−0.862	−0.862	−0.862	−0.862

TABLE 6: Selected Orbital Energies (au) of the 7 Molecules in the 4M Set

bond	N_8	N_{16}	N_{24}	N_{32}	N_{40}	N_{48}	N_{56}
$R_{1,2}$	−0.753	−0.758	−0.745	−0.739	−0.739	−0.742	−0.738
$R_{1,5}$	−0.753	−0.894	−0.909	−0.917	−0.917	−0.915	−0.917
$R_{5,6}$	−0.753	−0.830	−0.859	−0.850	−0.851	−0.851	−0.851
$R_{6,13}$		−0.894	−0.889	−0.890	−0.892	−0.892	−0.892
$R_{13,14}$		−0.758	−0.859	−0.921	−0.915	−0.917	−0.915

TABLE 7: Selected Orbital Energies (au) of the 3 Molecules in the 5M Set

bond	N_{10}	N_{20}	N_{30}	bond	N_{10}	N_{20}	N_{30}
$R_{1,2}$	−0.797	−0.840	−0.776	$R_{7,16}$		−0.840	−0.878
$R_{1,6}$	−0.761	−0.839	−0.900	$R_{16,17}$		−0.840	−0.848
$R_{6,7}$	−0.797	−0.840	−0.849	$R_{17,26}$			−0.900

TABLE 8: Selected Orbital Energies (au) of the 2 Molecules in the 6M Set

bond	N_{12}	N_{24}	bond	N_{12}	N_{24}
$R_{1,2}$	−0.795	−0.865	$R_{8,19}$		−0.805
$R_{1,7}$	−0.773	−0.803	$R_{19,20}$		−0.866
$R_{7,8}$	−0.795	−0.870			

The GEs via eq 7 and GHOFs via eq 8 are listed in Tables 15−18.

3. Results and Discussion

The geometrical optimizations were successfully completed (see Figures 1−4).The AIM analysis[25] based on the above structures has been performed to obtain the topological properties of the electron density, such as the Laplacian of ρ ($\nabla^2\rho$), the bond critical points (BCPs), ring critical points and cage critical points, the bond paths, ring paths, and cage paths. The $\nabla^2\rho$ identifies whether the charge of the region is locally depleted ($\nabla^2\rho > 0$) or concentrated ($\nabla^2\rho < 0$). The former is typically associated with interactions between closed-shell systems (ionic bonds, hydrogen bonds, and van der Waals molecules), whereas the latter characterizes covalent bonds, where the electron density concentrates in the internuclear region. Obviously, the latter is required for covalent bond formation. According to the principle of symmetry, parts of $\nabla^2\rho$ for BCP are listed in Tables 9−13. From these tables, one can find that $\nabla^2\rho$ for BCP are all less than 0.0. It indicates that all bonds in every molecule are covalent bonds. The number of BCPs (not listed) of molecule N_{2n} satisfies the formula $3n/2$, which indicates that each nitrogen atom has three covalent bonds. Meanwhile, "ellipticity" obtained from AIM analysis (not listed) shows that these bonds have σ_{N-N} bonding properties. That is, the molecules are cage molecules with only single bonds. Furthermore, this conclusion can be confirmed by NBO analysis.[24]

3.1. Geometry. The bond in cage molecules can be considered as the crossing line of two vicinal rings. So, the vicinal rings affect directly the properties of the bond. If the numbers of atoms in the rings on two sides of the bond are m ($m = 3-6$) and n ($n = 3-6$), respectively, the bond type is defined as ***mn*** ($m \leq n$) bond (abbreviated ***mn*B**) in this work. The partial bond lengths of molecules in the **3M** set are listed in Table 1. There are **34B**, **44B**, **35B**, **55B**, **56B**, and **66B** bonds in this set. N_6 is a special case, and its geometry structure is different from that of the others. Correspondingly, the bond lengths and the orbital energies (OE) are different from those of the others, too. The **34B** and **44B** exist in molecule N_6 only. The **34B** length is 1.481 Å ($R_{1,2}$ in Table 1), and the **34B** OE is −0.71557 au ($R_{1,2}$ in Table 5). The **44B** length is 1.524 Å ($R_{1,4}$ in Table 1), and the **44B** OE is −0.74770 au ($R_{1,4}$ in Table 5). The **35B** exists in all molecules of this set except N_6. In these molecules, the **35B** lengths are nearly invariable (the shortest one is 1.526 Å of N_{18}, and the longest one is 1.532 Å of N_{12}), and the OEs are quite close to each other (the lowest OE is −0.70877 au of N_{18}, and the highest one is −0.69790 au of N_{12}). The **55B** bonds also exist in all the molecules except N_6. Similar to **35B**, the **55B** lengths are nearly invariable in these molecules (the shortest bond length is 1.428 Å, and the longest one is 1.432 Å) except for the bonds in molecule N_{12}, in which there are two kinds of bond lengths, 1.420 Å and 1.494 Å, and the **55B** OEs are almost equal (the lowest OE is −0.90276 au of N_{12}, and the highest one is −0.89030 au of N_{18}). The **56B** exists in all the molecules except N_6 and N_{12}. The **56B** lengths are also almost constant in these molecules (the shortest bond length of this type is 1.477 Å, and the longest one is 1.484 Å), and the **56B** OEs are from −0.84452 au (N_{24}) to −0.84689 au (N_{30}). There are two types of **66B**. One type is the bonds linking the inserted hexagons, and another type is the bonds which form the inserted hexagon. The bond length of the latter is shorter (1.458 Å) than that of the former (1.483 Å or 1.492 Å). The **66B** OE of the latter is lower (−0.88309 au of N_{24}) than that of the former (−0.86459 au of N_{24}), respectively.

There are 5 kinds of bonds in the 7 molecules of **4M** set: **44B**, **45B**, **55B**, **56B**, and **66B**. The bond lengths of these molecules are listed in Table 2. The bond length of **44B** is 1.523 Å in N_8. The OE is −0.75260 au. The bond length is close to that of **44B** (1.524 Å) of N_6 in the **3M** set, and for **44B** there exists a small difference between the N_6 (−0.74770 au) and N_8 (−0.75260 au) OEs. The **55B** length of N_{24} in this set is 1.427 Å. It is close to that of the identical bonds in the **3M** set (average 1.428 Å), and the **55B** OE is slightly lower than that of the identical bonds in the **3M** set. The **56B** length of N_{24} in this set is 1.477 Å. It is close to that of the identical bonds in the **3M** set (average 1.482 Å). The **66B** length of N_{24} in this set is 1.468 Å. It is close to that of identical bonds in the **3M** set (average 1.479 Å). Similarly, The **44B** length in the **5M** set (see Table 3) and the **6M** set (see Table 4) are close to those of the identical bonds in the **3M** set. The **45B** lengths are close to those of the identical bonds in the **4M** set. The **55B** and the **56B** lengths of this type are close to those of the identical bonds in the **3M** set, too. The OEs have the same pattern in comparison with the bond lengths except that of the cage N_{20} in the **5M** set, of which molecule both the bond lengths (1.493 Å) and the OEs (−0.83959 au) are equal.

Just as discussed above, the bond lengths of the same type in the different molecules are almost invariable. The **55B** lengths are always the shortest and their OEs are the lowest in the

TABLE 9: Selected Laplacians of ρ ($\nabla^2\rho$) of Bond Critical Points of the 10 Molecules in the 3M Set

bond	N_6	N_{12}	N_{18}	N_{24}	N_{30}	N_{36}	N_{42}	N_{48}	N_{54}	N_{60}
$R_{1,2}$	−0.421	−0.238	−0.381	−0.378	−0.251	−0.247	−0.247	−0.248	−0.249	−0.248
$R_{1,4}$	−0.506	−0.634	−0.666	−0.668	−0.614	−0.619	−0.616	−0.617	−0.617	−0.617
$R_{4,5}$	−0.420	−0.426	−0.636	−0.634	−0.460	−0.456	−0.459	−0.457	−0.459	−0.455
$R_{5,10}$		−0.634	−0.647	−0.648	−0.499	−0.498	−0.497	−0.497	−0.497	−0.495
$R_{10,12}$		−0.238	−0.634	−0.621	−0.515	−0.519	−0.521	−0.519	−0.520	−0.521
$R_{12,16}$			−0.666	−0.650	−0.496	−0.494	−0.494	−0.494	−0.492	−0.492

TABLE 10: Selected Laplacians of ρ ($\nabla^2\rho$) of Bond Critical Points of the 7 Molecules in the 4M Set

bond	N_8	N_{16}	N_{24}	N_{32}	N_{40}	N_{48}	N_{56}
$R_{1,2}$	−0.504	−0.345	−0.298	−0.287	−0.295	−0.290	−0.280
$R_{1,5}$	−0.504	−0.553	−0.592	−0.603	−0.597	−0.600	−0.605
$R_{5,6}$	−0.504	−0.385	−0.399	−0.382	−0.388	−0.383	−0.381
$R_{6,13}$		−0.554	−0.494	−0.521	−0.525	−0.524	−0.524
$R_{13,14}$			−0.399	−0.493	−0.481	−0.487	−0.481
$R_{14,21}$				−0.521	−0.525	−0.531	−0.531

TABLE 11: Selected Laplacians of ρ ($\nabla^2\rho$) of Bond Critical Points of the 3 Molecules in the 5M Set

bond	N_{10}	N_{20}	N_{30}	bond	N_{10}	N_{20}	N_{30}
$R_{1,2}$	−0.466	−0.404	−0.243	$R_{7,16}$		−0.405	−0.439
$R_{1,6}$	−0.510	−0.403	−0.540	$R_{16,17}$		−0.405	−0.338
$R_{6,7}$	−0.466	−0.404	−0.339	$R_{17,26}$			−0.540

TABLE 12: Selected Laplacians of ρ ($\nabla^2\rho$) of Bond Critical Points of the 2 Molecules in the 6M Set

bond	N_{12}	N_{24}	bond	N_{12}	N_{24}
$R_{1,2}$	−0.419	−0.410	$R_{7,8}$	−0.419	−0.463
$R_{1,7}$	−0.533	−0.299	$R_{8,19}$		−0.304

TABLE 13: Parts of Nonlocalized Electron Numbers of Orbitals of the 10 Molecules in the 3M Set

bond	N_6	N_{12}	N_{18}	N_{24}	N_{30}	N_{36}	N_{42}	N_{48}	N_{54}	N_{60}
$R_{1,2}$	0.016	0.046	0.043	0.046	0.045	0.046	0.046	0.046	0.045	0.046
$R_{1,4}$	0.009	0.019	0.026	0.025	0.025	0.026	0.025	0.026	0.025	0.025
$R_{4,5}$	0.016	0.031	0.023	0.024	0.023	0.024	0.023	0.024	0.023	0.024
$R_{5,10}$		0.019	0.026	0.030	0.030	0.030	0.030	0.030	0.030	0.030
$R_{10,12}$		0.046	0.023	0.016	0.016	0.016	0.016	0.016	0.016	0.016
$R_{12,16}$			0.026	0.030	0.033	0.034	0.034	0.034	0.034	0.034

TABLE 14: Parts of Nonlocalized Electron Numbers of Orbitals of the 7 Molecules in the 4M Set

bond	N_8	N_{16}	N_{24}	N_{32}	N_{40}	N_{48}	N_{56}
$R_{1,2}$	0.009	0.031	0.032	0.034	0.034	0.033	0.034
$R_{1,5}$		0.023	0.025	0.024	0.024	0.024	0.024
$R_{5,6}$		0.033	0.026	0.027	0.027	0.026	0.027
$R_{6,13}$			0.024	0.027	0.027	0.027	0.027
$R_{13,14}$				0.016	0.015	0.015	0.016
$R_{14,21}$					0.031	0.030	0.030

TABLE 15: Total Energies E_0 (au), ΔH_f (kcal/mol), GE (au), and GHOF (kcal/mol) of the 10 Molecules at B3LYP/CC-PVDZ in the 3M Set

molecule	E_0	ΔH_f	GE	GHOF
N_6	−328.09588	306.5	−54.68265	51.1
N_{12}	−656.39250	485.6	−54.69937	40.5
N_{18}	−984.55407	749.7	−54.69745	41.7
N_{24}	−1312.71878	1011.9	−54.69662	42.2
N_{30}	−1640.87730	1278.2	−54.69591	42.6
N_{36}	−1969.03676	1543.8	−54.69547	42.9
N_{42}	−2297.19599	1809.5	−54.69514	43.1
N_{48}	−2625.35517	2075.4	−54.69490	43.2
N_{54}	−2953.51438	2341.1	−54.69471	43.4
N_{60}	−3281.67362	2606.9	−54.69456	43.4

TABLE 16: Total Energies E_0 (au), ΔH_f (kcal/mol), GE (au), and GHOF (kcal/mol) of the 7 Molecules at B3LYP/CC-PVDZ in the 4M Set

molecule	E_0	ΔH_f	GE	GHOF
N_8	−437.43047	427.2	−54.67881	53.4
N_{16}	−875.13867	679.4	−54.69617	42.5
N_{24}	−1312.63281	1066.1	−54.69303	44.4
N_{32}	−1750.15394	1435.7	−54.69231	44.9
N_{40}	−2187.66444	1812.4	−54.69161	45.3
N_{48}	−2625.17593	2188.7	−54.69117	45.6
N_{56}	−3062.68786	2564.5	−54.69085	45.8

TABLE 17: Total Energies E_0 (au), ΔH_f (kcal/mol), GE (au), and GHOF (kcal/mol) of the 3 Molecules at B3LYP/CC-PVDZ in the 5M Set

molecule	E_0	ΔH_f	GE	GHOF
N_{10}	−546.86529	485.2	−54.68653	48.5
N_{20}	−1093.90543	860.4	−54.69527	43.0
N_{30}	−1640.68064	1403.9	−54.68935	46.8

TABLE 18: Total Energies E_0 (au), ΔH_f (kcal/mol), GE (au), and GHOF (kcal/mol) of the 2 Molecules at B3LYP/CC-PVDZ in the 6M Set

molecule	E_0	ΔH_f	GE	GHOF
N_{12}	−656.16152	631.0	−54.68013	52.6
N_{24}	−1312.60071	1087.2	−54.69170	45.3

molecules. These indicate that the five-membered rings play an important role in the relative stability of cage molecules. The pentagons in molecules are responsible for enhancing thermal stabilities, while the **44B** lengths are the longest and their OEs are the highest except in the **34B** and **35B** in molecules. These indicate that four-membered rings (referred to as quadrangles) are responsible for weakening thermal stabilities of cage molecules. Though the **34B** and **35B** lengths are the longest and their OEs are the highest in molecules, they cannot be considered as the unstable factors because the nonlocalized electron numbers of **34B** and **35B** are the most in molecules (see Table 13 and Table 14, about 0.045 for **34B** and **35B**, while the others are about 0.009−0.034). As known, delocalization may lead to hyperconjugation interaction, and hyperconjugation interaction can enhance thermal stabilities of molecules. The existence of delocalization of orbitals renders the molecules which contain triangles more stable. Obviously, the triangle is the secondary factor in thermal stabilities of cage molecules. These conclusions are consistent with those of refs 15 and 21.

3.2. GEs, GHOFs, and Stabilities. As shown in Tables 15−18, the total energies and the enthalpy changes decrease with the number of atoms in the molecules, and the ΔH_f calculated using eq 2 increases with the number of atoms in the molecules. As an example, the ascending order of the ΔH_f of the **3M** set is $N_6 < N_{12} < N_{18} < N_{24} < N_{30} < N_{36} < N_{42} < N_{48} < N_{54} < N_{60}$. The ΔH_f of N_{12} (485.6 kcal/mol) is higher than that of N_6 (306.5 kcal/mol) and lower than that of N_{18} (749.7 kcal/mol). The stability of N_{12} would be more stable than that of N_{18} and much more unstable than that of N_6 if estimations were based on their ΔH_f. Just as mentioned in section 2, the relative stabilities of the molecules cannot be estimated simply by the total energies or the ΔH_f because the quantities of chemical element in the molecules are different. GE and GHOF are introduced in this work in order to estimate the relative stabilities of nonisomer molecules. So, the comparison results are reliable because the GE and the GHOF are the total energy and the ΔH_f of molecule N_{2n} divided by $2n$ and, consequently, the comparison benchmark of nonisomers are consistent.

In the **3M** set, the GE of N_6 is −54.68265 au and the GHOF is 51.1 kcal/mol. They are all the highest in the set. The same ascending orders of the GEs and the GHOFs are found: $N_{12} < N_{18} < N_{24} < N_{30} < N_{36} < N_{42} < N_{48} < N_{54} < N_{60} < N_6$. The order of relative stabilities of these molecules is $N_{12} > N_{18} > N_{24} > N_{30} > N_{36} > N_{42} > N_{48} > N_{54} > N_{60} > N_6$ estimated using the GEs and the GHOFs. That is, in this set, N_6 is the most unstable molecule and N_{12} is the most stable molecule in thermodynamics. It is commonly considered that the more layers are in a molecule, the more stable it is. On the contrary, the relative stabilities are slightly lowered with the increasing of layers except that of N_6. The reasons are that the GHOFs are increased with the increasing number of atoms and reduced with the increasing number of layers. Combining these two factors, the GHOFs of molecules in this set are increased slightly with the increasing number of layers or atoms. N_6 is the most unstable molecule in the set because the molecule does not contain a pentagon, which is the primary factor of stability of cage molecules according to Strout.[15,21] N_{12} is the most stable molecule in the set because the proportion of pentagons is the most in all of the molecules. With the increasing number of layers, the relative stabilities of the molecules approach each other. For instance, the GHOFs of N_{36}, N_{42}, N_{48}, N_{54}, and N_{60} are 42.9, 43.1, 43.2, 43.4, and 43.4 kcal/mol, respectively; they are almost equal. Especially, the GHOF of N_{54} equals that of N_{60} (43.4 kcal/mol). It can be predicted that the GHOFs of molecules N_{66}, N_{72}, N_{78}, ..., N_{6m} ($m > 10$) should be 43.4 kcal/mol approximately. This indicates that the relative stabilities of the molecules in the **3M** set are not sensitive to the layer numbers when the nitrogen cage molecules are large enough.

In the **4M** set, 7 molecules (N_8, N_{16}, N_{24}, N_{32}, N_{40}, N_{48}, N_{56}) have been examined at the level B3LYP/CC-PVDZ set. Similar to the **3M** set, the ascending order of the GHOFs (see Table 16) of these molecules is $N_{16} < N_{24} < N_{32} < N_{40} < N_{48} < N_{56} < N_8$. The order of relative stabilities estimated by the GHOFs are is $N_{16} > N_{24} > N_{32} > N_{40} > N_{48}, N_{56} > N_8$. The GHOFs of N_{24}, N_{32}, N_{40}, N_{48}, and N_{56} are 44.4, 44.9, 45.3, 45.6, and 45.8 kcal/mol, respectively. The GHOF difference of N_{32} and N_{24} is 0.5 kcal/mol, the GHOF difference of N_{40} and N_{32} is 0.4 kcal/mol, the GHOF difference of N_{48} and N_{40} is 0.3 kcal/mol, and the GHOF difference of N_{56} and N_{48} is 0.2 kcal/mol. It can be deduced that the GHOF difference of N_{64} and N_{56} should be smaller than that of any other formerly mentioned. That is, the relative stabilities of the molecules in the **4M** set are not sensitive to the layer numbers when the nitrogen cage molecules are large enough. The same conclusion can be drawn with respect to the **5M** set and the **6M** set.

As is known, the estimation of relative stabilities of isomers based on the ΔH_f and GHOF are equivalent. Among the 22 nitrogen cage molecules, N_{12} (D_{3d}) in the **3M** set and N_{12} (D_{6h}) in the **6M** set are the isomer molecules. The GHOF of the former (40.5 kcal/mol) is lower than that of the latter (52.6 kcal/mol), which indicates that the former is more stable than the latter. N_{24} (D_{3d}) in the **3M** set, N_{24} (D_{4h}) in the **4M** set, and N_{24} (D_{6d}) in the **6M** set are also the isomer molecules. The GHOF of N_{24} (D_{3d}) (42.2 kcal/mol) is lower than that of N_{24} (D_{4h}) (44.4 kcal/mol), while the latter is lower than that of N_{24} (D_{6d}) (45.3 kcal/mol). That is, the stability order is N_{24} (D_{3d}) > N_{24} (D_{4h}) > N_{24} (D_{6d}). The relative stabilities of isomers N_{30} (D_{3h}) (42.6 kcal/mol) in the **3M** set and N_{30} (D_{5h}) (46.8 kcal/mol) in the **5M** set have the same pattern. According to Strout et al.,[15,21] it is difficult to explain why the relative stability of N_{24} (D_{4h}) is higher than that of N_{24} (D_{6d}) because the former contains 2 quadrangles, which is the unstable factor of cage molecules, and 8 pentagons, which is the stable factor of cage molecules, while the latter contains 12 pentagons and has no quadrangle. This stability order should be attributed to the difference of layers in the isomers. The layers of N_{24} (D_{3d}), N_{24} (D_{4d}), and N_{24} (D_{6d}) are 8, 6, and 4 respectively (see Table 19). The layer number of N_{24} (D_{4d}) is more than that of N_{24} (D_{6d}).The GHOF of the N_{12} (D_{6h}) cage is the highest (52.6 kcal/mol) in Table 19 and contains the fewest layers (2 layers). While N_{24} (D_{3d}) and N_{30} (D_{3d}) contain more layers (8 and 10, respectively), the GHOFs are low (42.2 and 42.6 kcal/mol, respectively). So we can say that the layer also plays an important role in the stability of a molecule. Considering the conclusion of refs 15 and 21 that a cylindrical molecule is more stable than a spherical molecule, our conclusion is consistent with refs 15 and 21.

TABLE 19: The Relationship of Layers and ΔH_f (kcal/mol) of Isomers

	N_{12} (D_{3d})	N_{12} (D_{6h})	N_{24} (D_{3d})	N_{24} (D_{4h})	N_{24} (D_{6d})	N_{30} (D_{3h})	N_{30} (D_{5h})
layer	4	2	8	6	4	10	6
ΔH_f	485.6	631.0	1011.9	1066.1	1087.2	1278.2	1403.9
GHOF	40.5	52.6	42.2	44.4	45.3	42.6	46.8

4. Conclusion

In our work, 22 species of nitrogen cage molecules were selected to be investigated. The relative stabilities were studied from the bonding properties and the orders of energies of different forms including the total energies, the ΔH_f, the GEs, and the GHOFs. Our study focused on the relationship between the relative stabilities and the layer numbers. The results show the following: (i) For isomer cage molecules, the more layers there are in the molecules, the more stable the molecules are. That is, the cylindrical isomers of nitrogen cage molecules are more stable than the spherical ones. This conclusion is consistent with ref 21. (ii) For the nonisomer cage molecules, when n is great enough (for example, $n > 24$), the relative stabilities of these large cage molecules tend to be the same. (iii) The GHOFs increase with increasing number of atoms and reduce with increasing number of layers. Combining these two factors, the GHOFs of molecules are increased slightly with the increasing number of layers or atoms. That is, layers are also the stable factor of cage molecules.

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