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What Makes the Cylinder-Shaped N_{72} Cage Stable?

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Recent theoretical studies have suggested that the stabilizing factors for large nitrogen cages tend to favor more five-membered rings, more three-membered rings, and cylindrical structures with large numbers of layers. One of the major issues in this study of the all-nitrogen molecule is the determination of what brings about the stabilizing factors. Herein, the cylinder-shaped molecule of N_{72} (D_{3d}) has been studied in detail. The geometry and energies are examined at B3LYP/cc-pVDZ, and single-point energy calculations at MP2/cc-pVDZ are carried out for the purposes of determining relative thermodynamic stability. Natural bond order (NBO) analysis and atoms in molecules (AIM) analysis are applied to investigate the bonding properties of the cage molecule. The major result of this study is the identification of intramolecular interactions, whether it is at B3LYP/cc-pVDZ or at MP2/cc-pVDZ, as the dominant stabilizing factor for the large all-nitrogen cage. The length of the cylinder-shaped molecule is about 2.2 nm. N_{72} (D_{3d}) might be one novel nanomaterial which is environment friendly, and as a beeline nanotube or a beeline "nano-bar", it is expected to impact a wide range of applications.

1. Introduction

Molecules containing only nitrogen atoms have come under recent scrutiny as candidates for high-energy density materials (HEDMs),[1−22] due to the dissociation of the all-nitrogen 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 considered a viable candidate for HEDM, all-nitrogen molecules need to possess a resistance to decomposition to some extent. The difficulty lies in estimating all-nitrogen molecules that are metastable enough to serve as stable fuels. So, the relative stabilities of all-nitrogen molecules have become the focus of recent experimental and theoretical research. The stabilities of an even number of atoms N_{2n} molecules have been studied in a computational survey of various structural forms with up to 60 atoms. Cyclic, acyclic, and cage isomers have been studied to examine the bonding properties and energy properties over a wide range of molecules, 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},[9,21,22] N_{30},[11,21,22] N_{32},[22] N_{36}[21,22] N_{40},[22] N_{42},[22] N_{48},[22] N_{54},[22] N_{56},[22] and N_{60}.[11,22] The computational studies of cage isomers of N_{12},[15] N_{24},[21] N_{30},[21] and N_{36}[21] examined specific structural features that lead to the most stable molecules among the three-coordinate nitrogen cages. Those results showed that molecules with the most five-membered rings (referred to as pentagons) in the nitrogen network tend to be the most stable, with a secondary stabilizing effect due to three-membered rings (referred to as triangles) in the cage structure. Meanwhile, Strout et al.[21] have pointed out that the cylinder-shaped nitrogen cages are more stable than the other shape. Our recent theoretical predictions on cage stability for 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}))[22] indicate that the most thermodynamically stable isomer has 3-fold symmetry (D_{3h} or D_{3d} symmetry point group). Such molecules have a triangle−pentagon bonding group on each end with a band of hexagons around the midsection. However, the existence of this symmetric cage depends on the number of nitrogen atoms being a multiple of three or on the number of layers. Besides these factors, are there any other factors which render the cylinder-shaped nitrogen cage to be stable? Such reports have not been seen. Cage N_{72} (D_{3d}), which is the largest nitrogen cage investigated until now, with these features has never studied before as well.

2. Methods

For the convenience of constructing the cage N_{72} (D_{3d}), the concept of "layer" is introduced in this work. The term "layer" can be defined as (i) all atoms belonging to the same layer are coplanar, (ii) all layers in one molecule are parallel to each other, and (iii) all planes in one molecule are perpendicular to its C_3 principal axis. According to this definition, the layers of the molecule and the atoms in each layer of the molecule are shown in Figure 1.

The molecule N_{72} (D_{3d}) can be constructed by the manner of ref 22: At first, the N_6 (D_{3h}) cage molecule is chosen as the mother molecule. N_6 (D_{3h}) has two parallel layers called the top layer and the bottom layer, respectively. Then, one W-shaped (chair-form) six-membered ring (referred to as hexagon) is inserted into the mother molecule. The atoms in the hexagon link to the atoms in the top layer and link to the atoms in the bottom layer of the mother molecule in an alternating manner. Thus, the cage molecule N_{12} (D_{3d}) is formed. In the molecule N_{12} (D_{3d}), the three atoms in the hexagon linking to the top layer atoms of the mother molecule form one layer and the remaining three atoms in the hexagon linking to the bottom layer atoms form another one. There are four layers in molecule N_{12} (D_{3d}). Analogously, the cage molecule N_{18} (D_{3h}) can be

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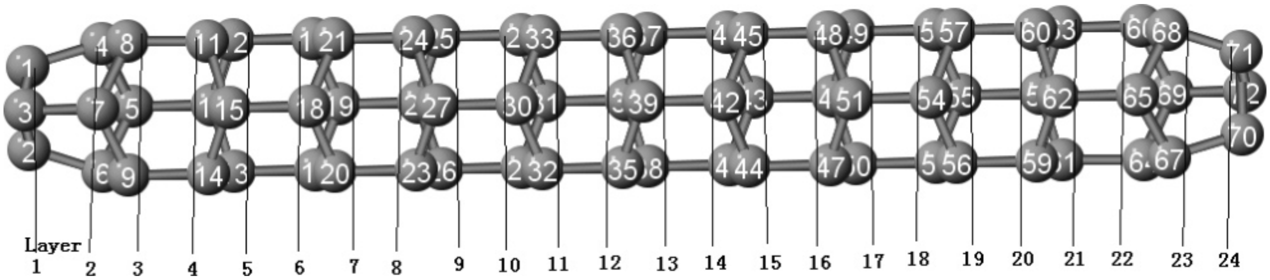

Figure 1. Structure and the layers of the N_{72} (D_{3d}) cage at B3LYP/cc-pVDZ.

TABLE 1: Covalent Bonds or Intramolecular Interactions in Every Set of the N_{72} (D_{3d}) Cage at B3LYP/cc-pVDZ

type	number[a]	bond
35B	6	N1−N2, N1−N3, N2−N3, N70−N71, N70−N72, N71−N72
55B	6	N1−N4, N2−N6, N3−N7, N67−N70, N68−N71, N69−N72
56B	12	N4−N5, N4−N8, N5−N6, N6−N9, N7−N8, N7−N9, N64−N67, N64−N69, N65−N67, N65−N68, N66−N68, N66−N69
66B1	30	N5−N10, N8−N11, N9−N14, N12−N16, N13−N17, N15−N18, N19−N22, N20−N23, N21−N24, N25−N28, N26−N29, N27−N30, N31−N34, N32−N35, N33−N36, N37−N40, N38−N41, N39−N42, N43−N46, N44−N47, N45−N48, N49−N52, N50−N53, N51−N54, N55−N58, N56−N59, N57−N60, N61−N64, N62−N65, N63−N66
66B2	54	N10−N12, N10−N13, N11−N12, N11−N15, N13−N14, N14−N15, N16−N19, N16−N21, N17−N19, N17−N20, N18−N20, N18−N21, N22−N25, N22−N26, N23−N26, N23−N27, N24−N25, N24−N27, N28−N31, N28−N33, N29−N31, N29−N32, N30−N32, N30−N33, N34−N37, N34−N38, N35−N38, N35−N39, N36−N37, N36−N39, N40−N43, N40−N45, N41−N43, N41−N44, N42−N44, N42−N45, N46−N49, N46−N50, N47−N50, N47−N51, N48−N49, N48−N51, N52−N55, N52−N57, N53−N55, N53−N56, N54−N56, N54−N57, N58−N61, N58−N63, N59−N61, N59−N62, N60−N62, N60−N63
V1[b]	6	N4−N12, N6−N13, N7−N15, N58−N69, N59−N67, N60−N68
V2	24	N10−N19, N14−N20, N11−N21, N16−N25, N17−N26, N18−N27, N22−N31, N23−N32, N24−N33, N28−N37, N29−N38, N30−N39, N34−N43, N35−N44, N36−N45, N40−N49, N41−N50, N42−N51, N46−N55, N47−N56, N48−N57, N52−N63, N53−N61, N54−N62
LP1	6	N1, N2, N3, N70, N71, N72
LP2	6	N4, N6, N7, N67, N68, N69
LP3	6	N5, N8, N9, N64, N65, N66
LP4	54	N10 ∼ N63

[a] The number of bonds or van der Weals interactions or lone pairs in every set of the molecule. [b] The intramolecular interactions V1 vanish at MP2/cc-pVDZ.

considered as two hexagons with 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}), N_{60} (D_{3d}), N_{66} (D_{3h}), and N_{72} (D_{3d}) can be formed in the same way. So, cage molecule N_{72} (D_{3d}) can be regarded as the derivative of 11 hexagons being inserted into the mother molecule. Two new layers are added when one W-shaped hexagon is inserted into the mother molecule. Thus, the molecule N_{72} (D_{3d}) contains 24 layers. Each layer contains three nitrogen atoms. The atoms in the same layer are not conjoined and only join to the atoms of the previous layer and the next layer except layer 1 and layer 24.

We have carried out theoretical studies of the N_{72} (D_{3d}) cage using the Gaussian 98 A.11 packages.[23] Density functional theory (DFT) has been applied to optimize the structures of N_{72} (D_{3d}) at the basis set cc-pVDZ. The single-point energies of the molecule have been carried out at MP2/ cc-pVDZ to obtain the wave functions. The optimized structure of N_{72} (D_{3d}) at B3LYP/cc-pVDZ is shown in Figure 1.

The bond in the cage molecule can be considered as the crossing line of two vicinal rings. So, the vicinal rings on two sides of the crossing line directly affect the bonding properties. 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, then the bond type is defined as the **mn** (**m** ≤ **n**) bond (ab. **mnB**) in this work. There are five sets of bonds in the cage molecule N_{72} (D_{3d}), **35B**, **55B**, **56B**, **66B** (**66B1**, **66B2**); two sets of intramolecular interactions, denoted by **V1** and **V2**, respectively; four sets of lone pairs, denoted by **LP1**, **LP2**, **LP3**, and **LP4**, respectively. The bonds or the intramolecular interactions or the lone pairs in every set are listed in Table 1. It is noted that the bonding properties are equivalent in the same set. The geometrical parameters are listed in Table 2.

TABLE 2: Covalent Bond Length and Orbital Energies (atomic units) of the N_{72} (D_{3d}) Cage at B3LYP/cc-pVDZ

	length (Å)	occupancy[a]	OE	TSEE[b]
35B (N1−N2)	1.529	1.954	−0.70761	31.8
55B (N1−N4)	1.427	1.975	−0.89830	−1.1
56B (N4−N5)	1.483	1.976	−0.84692	1.6
66B1 (N5−N10)	1.483	1.970	−0.86792	−6.3
66B2 (N10−N12)	1.460	1.984	−0.88315	−0.9
LP1(N1)		1.952	−0.58233	−20.4
LP2(N4)		1.893	−0.49975	0.4
LP3(N5)		1.924	−0.49022	−3.2
LP4(N10)		1.913	−0.47716	3.0

[a] Electron occupancy of orbital. [b] Occupied NLMO contributions dE(i) (kcal mol^{-1}) to total steric exchange energy.

The topological properties of bonds in molecules have a significant influence on the thermodynamic stability of the molecule. So, natural bond orbital (NBO) analysis[24] and atoms in molecule (AIM) analysis[25] are carried out to study the bonding properties. The orbital energies, occupancies, and the steric exchange energies from NBO analysis are listed in Table 2.

AIM analysis 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), the ring critical points,

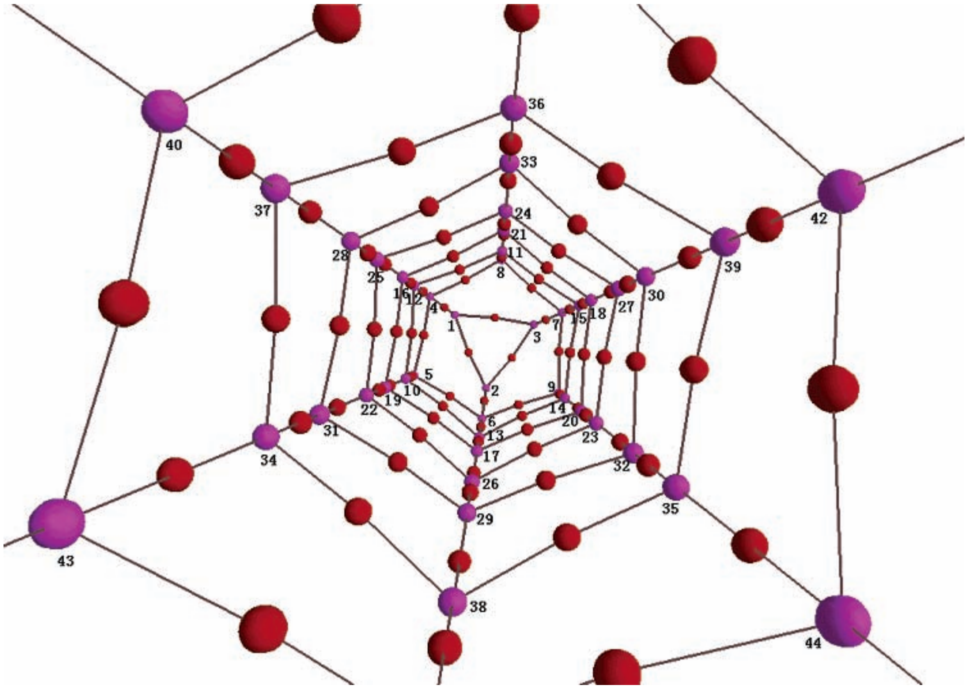

Figure 2. Parts of the BCPs (the unmarked balls) and the bond paths (lines) of the N_{72} (D_{3d}) cage at B3LYP/cc-pVDZ viewed from the *X*-axis direction. The atoms are marked by digits. There are three intramolecular interactions between layers 2 and 5 and three intramolecular interactions between layers 22 and 25 at B3LYP/cc-pVDZ. These six intramolecular interactions do not exist at MP2/cc-pVDZ.

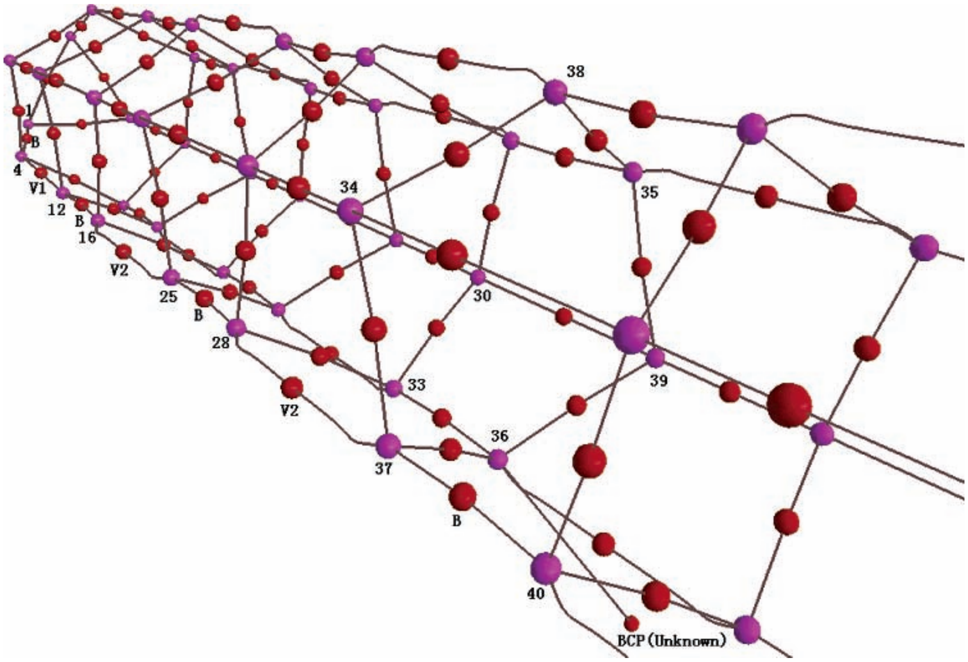

Figure 3. Parts of the BCPs and the bond paths (lines) of the N_{72} (D_{3d}) cage at B3LYP/cc-pVDZ viewed from the flank of *X*-axis. The atoms are marked by digits. **B** represents the BCP of covalent bond, and **V** represents the intramolecular interactions. There are three intramolecular interactions between layers 2 and 5 and three intramolecular interactions between layers 22 and 25 at B3LYP/cc-pVDZ. These six intramolecular interactions do not exist at MP2/cc-pVDZ.

and the cage critical points, and the bond paths, the ring paths, the cage paths, and the distances between the BCPs and the atoms. 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. The bonding characteristic can be described by the "ellipticity" (ϵ) of the bonds, where the greater ϵ is, the more π component the bond has; the less ϵ is, the more σ component the bond has. Bond intensity can be measured by the electron density (ρ) of the BCP, where the greater ρ is, the more intension the bond is. The bond critical points (BCPs) and bond paths in AIM analysis are shown in Figure 2 and Figure 3. The cylinder-shaped cage is too long in the *X*-axis direction to be illustrated in the AIM view window as a whole molecule. Figure 2 is the front view of the *X*-axis direction, and Figure 3 is the side view of the *X*-axis direction in three-dimensions. The

TABLE 3: Ellipticity (ϵ), Electron Density (ρ) and the Laplacian ($\nabla^2\rho$) of the N_{72} (D_{3d}) Cage at B3LYP/cc-pVDZ

	dist. 1[a]	dist. 2[b]	ϵ	ρ	$\nabla^2\rho$
35B (N1−N2)	0.766	0.766	0.183	0.247	−0.247
55B (N1−N4)	0.709	0.720	0.105	0.323	−0.618
56B (N4−N5)	0.739	0.745	0.107	0.285	−0.457
66B1 (N5−N10)	0.740	0.745	0.199	0.282	−0.498
66B2 (N10−N12)	0.729	0.731	0.086	0.300	−0.519
V1(N4···N12)[c]	1.207	1.211	3.109	0.024	0.143
V2(N16···N25)	1.168	1.168	0.048	0.030	0.161
66B2 (N36−N39)	0.732	0.732	0.091	0.298	−0.515
N36···N39[c]	3.433	3.598	9677.373	6×10^{-9}	2×10^{-7}

[a] The distance between the BCP and the first atom. [b] The distance between the BCP and the second atom. [c] These intramolecular interactions do not exist at MP2/cc-pVDZ.

distances between the BCP and atom pairs, ϵ, ρ, and $\nabla^2\rho$ of BCPs from AIM analysis of the molecule N_{72} (D_{3d}) are listed in Table 3.

3. Results and Discussion

The geometrical optimizations were successfully completed (see Figure 1) at the B3LYP/cc-pVDZ level. All of the vibrational frequencies of the molecule are positive. The lowest vibrational frequency is 30 cm^{-1}. That is, the molecule structure of N_{72} (D_{3h}) is a local minimum at the B3LYP/cc-pVDZ potential energy surface. The results from NBO analysis show that the molecule has 108 σ_{N-N} covalent bonds. That is, the molecules are cage molecules with only single bonds. The results from AIM analysis (see Table 3) show that the $\nabla^2\rho$ values of the BCP, of which the distances between the BCPs and atoms are less than 0.8 Å (0.8 Å is the threshold value specified by us because the length of the covalent bond should be less than $2 \times 0.8 = 1.6$ Å at B3LYP/cc-pVDZ), are less than 0.0. It indicates that the bonds in the molecule are covalent bonds. The number of BCPs, which $\nabla^2\rho < 0$ satisfies with the formula $3 \times 72/2 = 108$, indicates that each nitrogen atom has three covalent bonds. Meanwhile, the ϵ value obtained from AIM analysis shows that these bonds have σ_{N-N} bonding characteristics. The results from AIM analysis also show that the molecule has 30 + 1 intramolecular interactions at B3LYP/cc-pVDZ and 24 intramolecular interactions at MP2/cc−pVDZ because $\nabla^2\rho > 0$ for the BCPs. It is noted that the B3LYP functional does not address intermolecular van der Waals interactions well because of its missing long-range correction (LC) for generalized gradient approximation (GGA) exchange[26,27] functionals. So, the single-point energy calculations of the molecule at MP2/cc-pVDZ have been carried out to verify the existence of intramolecular interactions. The results show that there are 24 intramolecular interactions in the molecule at MP2/cc-pVDZ. Three intramolecular interactions between layer 2 and layer 5 and three intramolecular interactions between layer 20 and layer 23, which can be observed at B3LYP/cc-pVDZ, are not found at MP2/cc-pVDZ. The remaining 24 intramolecular interactions at MP2/cc-pVDZ are the same as they are at B3LYP/cc-pVDZ. Furthermore, these intramolecular interactions are relatively "strong" because the interaction distances are short (about 2.3 Å at B3LYP/cc-pVDZ and MP2/cc-pVDZ). In this case, the intramolecular interactions can be treated with B3LYP as with MP2.

N1−N2 is a typical **35B** bond. The bond length is the longest (1.529 Å, see Table 2) and the orbital energy (OE) from NBO analysis is the highest (−0.70761 au, see Table 2) in the molecule. Meanwhile, the electron occupancy of the orbital is the lowest (1.954, see Table 2). N1−N2 tends to be somewhat a π bond from the point of view of its ϵ value (0.183, see Table 3). The $\nabla^2\rho$ is −0.247, which indicates that the bond is a covalent bond. N1−N2 is a stronger covalent bond because the BCP has higher electron density (ρ of the BCP is 0.247). The fact that the bond length is the longest and the OE is the highest in the molecule may be caused by steric repulsions. It can be confirmed by the total steric exchange energy (referred to as TSEE, 31.8 kcal mol^{-1}, see Table 2) from NBO analysis. The existence of steric repulsions can weaken the bond, and it transfers to lower the relative stability of the molecule. On the other hand, because the bond tends to be somewhat a π bond, the bond intensity is increased and it transfers to increase the stability of the molecule. The TSEE of the lone pair of N1 is −20.4 kcal mol^{-1} (**LP1** in Table 2), and it is the lowest in the molecule. This means that the repulsion of the lone pair of atom N1 is the least. The lone pair of atom N1 contributes to the intensity of the bonds between atom N1 and the other atoms. The interactions of lone pairs of atoms N1 and N2 make N1−N2 tend to be a double bond. At the same time, the N1−N2 bond is a crossing line between a triangle and a pentagon. The fact that the triangles are the stabilizing factor[15,21] of nitrogen cages may be caused by the π bond properties of this type of bond.

N1−N4 is a typical **55B** bond. The bond length is the shortest (1.427 Å) and the orbital energy (OE) from NBO analysis is the lowest (−0.89830 au) in the molecule. Meanwhile, the electron occupancy of the orbital is 1.975, which indicates that the number of nonlocalized electrons is small (2.0 − 1.975 = 0.025). N1−N4 is a covalent bond because its $\nabla^2\rho$ is −0.618 which is less than 0.0. The ρ value of the BCP is 0.323; it is the greatest among all of the electron densities (column ρ in Table 3), which indicates that the BCP has the highest electron density and the covalent bond is strongest in the molecule. The TSEEs of the N1−N4 bond (−1.1 kcal mol^{-1}) and the lone pairs of atoms N1 (−20.4 kcal mol^{-1}) and N4 (0.4 kcal mol^{-1}) are low; these may contribute to shorten the bond length and lower the OE. Meanwhile, the electron occupancy of the lone pair of N4 is the lowest (1.893) among all of the electron occupancies (column "occupancy" in Table 2). As defined above, the number of nonlocalized electrons is the greatest (2.0 − 1.893 = 0.107). The nonlocalized electrons make the bonds between atom N4 and the other atoms strengthen. At the same time, the N1−N4 bond is a crossing line between two vicinal pentagons. The fact that the pentagon is the dominant stabilizing factor[15,21] of nitrogen cages may be caused by the nonlocalized electrons of the lone pairs of atoms in the rings.

The properties of **56B** and **66B1** bonds are similar. **56B** bonds only exist in the ends of the cylinder (between layer 2 and layer 3 and layer 22 and layer 23). The **66B1** bonds are parallel to the C_3 principal axis approximately, such as the N5−N10 bond, while the **66B2** bonds, such as the N10−N12 bond, are not. It brings about some differences between the two kinds of bonds. The bond length of N5−N10 is 1.483 Å. It is longer than that of N10−N12 (1.460 Å). The OE of N5−N10 is −0.86792 au. It is higher than that of N10−N12 (−0.88315 au). On the other hand, the TSEE of the N5−N10 bond (−6.3 kcal mol^{-1}) is lower than that of the N10−N12 (−0.9 kcal mol^{-1}), which means that the repulsion action of the N5−N10 bond with the other orbitals is lower than that of the N10−N12 bond. The nonlocalized electrons of the N5−N10 bond (2.0 − 1.970 = 0.030) are greater than that of the N10−N12 (0.016), which means that the N5−N10 bond has a higher delocalization than that of N10−N12 bond. The delocalization contributes to the stability of the cage molecule. AIM analysis shows that there are 30 +

1 intramolecular interactions at B3LYP/cc-pVDZ and 24 intramolecular interactions at MP2/cc-pVDZ (see Table 1 and Figure 2) in the molecule. The intramolecular interactions only exist in the regions where the two atoms belong to different layers, the layer interval is 3 and the intramolecular interactions are approximately parallel to the C_3 principal axis. Take, for example, the intramolecular interaction N16···N25, where the atom N16 is in layer 6 (see Figures 1 and 3) and atom N25 is in layer 9. The difference of the two layers is 3, and N16···N25 is approximately parallel to the C_3 principal axis. In the direction of the C_3 principal axis, the intramolecular interactions conjoin with the **66B1** covalent bond in an alternating manner (e.g., N4···N12−N16···N25−N28···N37, where N4···N12 does not exist at MP2/cc-pVDZ) and form a quasi beeline. There are six such beelines in the molecule. All the beelines are approximately parallel to the C_3 principal axis (see Figure 3). The intramolecular interaction N4···N12 (denoted by **V1** in Figure 3) is near the ends of the cylinder, while the intramolecular interaction N16···N25 (denoted by **V2** in Figure 3) lies in the midsection of the cylinder. AIM analysis shows that the distance between the two atoms N4 and N12 and the BCP is about 1.21 Å, that is, the bond path of N4···N12 is about 2.42 Å at B3LYP/cc-pVDZ (see Table 3). The distance between the two atoms N16 and N25 and the BCP is about 1.17 Å both at B3LYP/cc-pVDZ and at MP2/cc-pVDZ, that is, the bond path of N16···N25 is about 2.34 Å. The ρ of the interaction N4···N12 is 0.024 at B3LYP/cc-pVDZ, and it is lower than that of the interaction N16···N25 ($\rho = 0.030$) at the same level. Both the difference of distances and the difference of the ρ between N4···N12 and N16···N25 indicate that the interaction of the former is weaker than that of the latter. Especially, the ϵ of the interaction N4···N12 (3.109) is much greater than that of N16···N25 (0.048) at B3LYP/cc-pVDZ, which means that the electrons scatter out of the region of the beeline between atom N4 and atom N12, while gather together in the region of the beeline between atom N16 and atom N25. This can be verified by the results of AIM analysis at MP2/cc-pVDZ. In such a case, the BCP between the atoms N4 and N12 vanishes; at the same time, the intensity of the intramolecular interaction between atoms N16 and N25 should be invariable at B3LYP/cc-pVDZ and MP2/cc-pVDZ because the interaction distance (2.35 Å at MP2/cc-pVDZ vs 2.34 Å at B3LYP/cc-pVDZ) and the electron density (0.028, which is not listed, at MP2/cc-pVDZ vs 0.030 at B3LYP/cc-pVDZ) are almost equal to each other. This indicates that B3LYP should be used to address the intramolecular interactions as MP2. Every two layers have three such interactions from layer 2 to layer 23 at B3LYP/cc-pVDZ and from layer 4 to layer 21 at MP2/cc-pVDZ. Such interactions strengthen the bonds of **56B** and **66B** and consequently make the cage molecule stable. The intramolecular interactions contribute to the relative stabilities of the cylinder-shaped molecule. This renders the molecule to be much more stable than if it does not occur.

All-nitrogen molecules N_{72} (D_{4d}) and N_{72} (D_{6d}) are the cage isomers of N_{72} (D_{3d}) with cylinder-shaped structures. Eighteen layers are in the molecule N_{72} (D_{4d}) and 12 layers are in the molecule N_{72} (D_{6d}). There were at most $(18 - 4) \times 2 = 28$ intramolecular interactions in the molecule N_{72} (D_{4d}) and $(12 - 4) \times 3 = 24$ intramolecular interactions in the molecule N_{72} (D_{6d}), while cage N_{72} (D_{3d}) contains $[(24 - 4) \times 3]/2 = 30$ intramolecular interactions in the molecule at B3LYP/cc-pVDZ. It is expected that the relative stability of cage N_{72} (D_{3d}) is higher than that of cages N_{72} (D_{4d}) and N_{72} (D_{6d}). The fact that the structure optimizations of cages N_{72} (D_{4d}) and N_{72} (D_{6d}) cannot be completed successfully is the best illustration of this point. The different relative stabilities between N_{72} (D_{3d}) and N_{72} (D_{4d}) and N_{72} (D_{6d}) are mainly caused by the unequal numbers of intramolecular interactions in the molecules. That is, intramolecular interactions are the dominate stabilizing features for all-nitrogen molecules.

Quite surprisingly, it is found that, at B3LYP/cc-pVDZ, there is an extra BCP which is far-off the cylinder of the molecule. The ϵ value of the BCP is much greater (9677.373). The ρ (6×10^{-9}, see Table 3) and the $\nabla^2\rho$ (2×10^{-7}) values are near to zero. The distances between the BCP and atoms N30, N33, N36, and N39 are 3.908, 3.643, 3.433, and 3.598 Å, respectively. It should be the BCP between atom N36 and atom N39, judging by the distances. But, N36−N39 is already judged as a **66B2** covalent bond by the properties of the BCP between atom N36 and atom N39. But, at MP2/cc-pVDZ, there is no such BCP. Where does the extra BCP come from and what actions does it take on the relative stabilities of the molecule at B3LYP/cc-pVDZ? These two points still remain a puzzle.

The enthalpy change is −3937.95263 au; the total energy is −3937.99205 au. The DFT ΔH_f [25] is 3138.5 kcal mol^{-1}. By means of the method of ref 22, the DFT group ΔH_f is about 43.5 kcal mol^{-1}, where the DFT group ΔH_f is the DFT ΔH_f divided by atom number 72. It is much closer to the 43.4 kcal mol^{-1} which is our prediction value in ref 22.

Our study shows that N_{72} (D_{3d}) is a beeline molecule. The length of the cylinder-shaped molecule is about 2.2 nm. This molecule might be one novel nanomaterial which is environment-friendly, and as a beeline nanotube or a beeline "nanobar", it is expected to impact a wide range of applications.

4. Conclusion

The results of this study show that the nitrogen cage N_{72} (D_{3d}) is metastable thermodynamically. The pentagons are the primary structural features that contribute to the stability of the molecules. Triangles in the molecular structure have a secondary stabilizing effect on the N_{72} (D_{3d}) cages. The cylinder-shaped structure of the all-nitrogen cage N_{72} (D_{3d}) is one of the stabilizing factors. These trends agree with the results of Strout et al.[15,21] Our studies show that the number of nitrogen atoms and the number of the intramolecular interactions are contrary stabilizing factors for the nitrogen cages, that is, the relative stabilities of the cage molecules are lowered with the increasing of number of atoms and increased with the increasing of number of intramolecular interactions in the molecules. All of the positive stabilizing factors are caused by the nonlocalization of lone pairs in the triangles and by the intramolecular interactions of nitrogen atoms in the different layers, where the intramolecular interactions are the dominant stabilizing feature of the molecule.

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