

Stability and Electronic Properties of Nitrogen Nanoneedles and Nanotubes

Jenna L. Wang,^{†,‡} Gerald H. Lushington,[‡] and Paul G. Mezey^{*,†,§}

Scientific Modeling and Simulation Laboratory (SMSL), Department of Chemistry and Department of Physics and Physical Oceanography, Memorial University of Newfoundland, St. John's, Newfoundland A1B 3X7, Canada, Molecular Graphics and Modeling Laboratory, University of Kansas, Lawrence, Kansas 66045, and Institute for Advanced Study, Collegium Budapest, Szentháromság utca 2, 1014 Budapest, Hungary

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The electronic structures and stability of nitrogen nanostructures, nanotubes, and fiberlike nanoneedles of various diameters, formed by units N_{2m} ($m = 2-6$), were studied by quantum chemistry computational modeling methods. The geometrical structures with various cross-sections and terminal units, their energetic stability, and their rather peculiar electron density distributions were investigated. The tightest nitrogen nanoneedle (NNN) studied theoretically in this work is the structure $(N_4)_n$ with D_{2h} symmetry, whereas the nitrogen nanotube (NNT) with the largest diameter discussed here is the structure $(N_{12})_n$ with D_2 symmetry. These families of NNNs and NNTs can be considered as nanostructures not only for potential applications as devices in nanotechnology or as possible scaffold structures but also as ligands in synthetic chemistry and high-energy density materials (HEDMs). As a consequence of the lone-pair electrons present around the walls of these NNNs and NNTs, these nitrogen nanostructures and the nitrogen nano-bundles (NNB) formed by aligning and combining them using intermediate carbon atoms, can have highly variable electronic properties controlled by the changing charge environment. In particular, for extended systems based on the units studied here, the band gaps of each of these systems can be affected greatly by the local charge of the environment.

I. INTRODUCTION

Based on their remarkable strengths and elasticities and on their highly anisotropic shapes as well as on a wide range of unique electronic, optical, and mechanical properties of carbon nanostructures (CNS),¹ these structures have found numerous applications in chemistry and physics. The initial report of graphitic microtubules by Iijima in 1991² and the discovery of single-walled carbon nanotube (SWNT) in 1993^{3,4} have motivated an extensive search for additional, similar structures. The results on carbon nanostructures have provided important suggestions concerning the possibilities of analogous systems built from non-carbon species and have led to investigations into whether analogous nitrogen nanostructures exist or not. The significant difference between carbon clusters and nitrogen clusters is that sheet graphite is one type of stable form of carbon, but nitrogen clusters prefer to form zigzag surfaces due to a distinct nitrogen electronic structure involving lone pairs. Nitrogen clusters dominated by N–N single bonds usually have very high energies because of the large difference in bond energies between the bonds of N–N and N≡N. The N–N single bond has a bond energy of 39 kcal/mol, while that for N=N is 100 kcal/mol, and N≡N has a bond energy of 228 kcal/mol at 298 K.⁵ Consequently, storing the maximum amount of energy in a polynitrogen molecule would mean having the largest number of single bonds. However, the nitrogen lone

pairs repel each other, and the single bonds are much weaker than, for example, a carbon–carbon single bond. Although N–N single bonds store more energy, the stability of such molecules against dissociation requires that they must also have some additional stabilizing features, for example, a minimum number of double bonds.

The initial expectations for the existence of nitrogen nanostructures analogous to the most prominent forms of carbon nanostructures were rather limited. Even in the size-range of small molecules, there are only a few all-nitrogen chemical species known experimentally, for instance, N_2 , N_3^{1-} ,⁶ N_5^{+} ,^{7,8} and N_5^{-} .⁹ Other species have been observed only as free gaseous or matrix-isolated ions or radicals, such as N_3^+ , N_3^+ , and N_4^+ .^{10–13} As discussed above, the N–N single-bond energy is much less than one-third of the triple-bond energy or one-half of the double-bond energy, and most homonuclear polynitrogen structures are thermodynamically highly unstable, having highly endothermic heats of formation, that explains why so few such structures are known.

However, these observations, by themselves, have not discouraged the search for additional structures. To meet this challenge, many theoretical studies have been carried out in search of new types of nitrogen clusters. The clusters CN_x have been studied by Hammerl and Klapötke^{14,15} both experimentally and theoretically. Gagliardi and Pyykkö¹⁶ designed and calculated the structures of ScN_7 and N_5 –metal– N_7 and their dissociation pathways. Nitrogen cages N_8 , N_{12} , and N_{18} were reported in Douglas groups' work.^{17,18} The sandwich-like structures of aromatic rings were also investigated by Mercero and co-workers.¹⁹ Some nitrogen-rich sulfides $S(N_3)_m$ ²⁰ and $S(N_4)_m$ ²¹ and their stability as well as the ionic

* Corresponding author phone: (709)737-8768; fax: (709)737-3702; e-mail: paul.mezey@gmail.com.

[†] Memorial University of Newfoundland.

[‡] University of Kansas.

[§] Collegium Budapest.

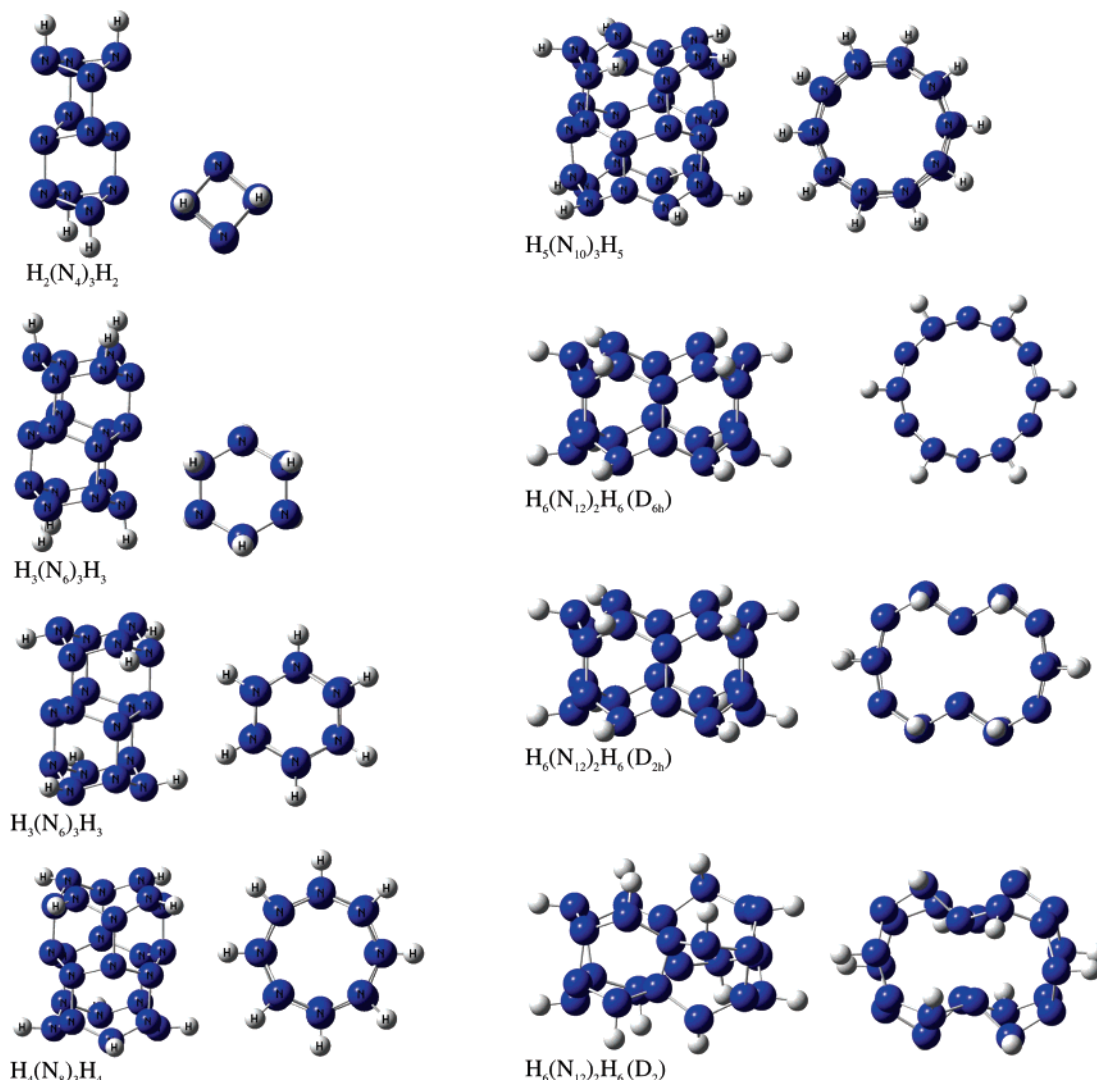


Figure 1. Nitrogen nanostructures formed by units of N_{2m} ($m = 2-6$) and terminated by hydrogen atoms (views from side and top).

compounds HN_8^+ ,²² $N_4H_2F^+$,²³ and $N_7H_2^+$ ²⁴ have also been studied. Additional new types, helical all-nitrogen and helical nitrogen-rich fused-ring clusters were also studied in our recent work.²⁵

In this paper, we report additional new structures, showing not only certain analogies but also fundamental differences when compared to carbon nanostructures. In particular, the geometrical structures, stability, electronic properties of nitrogen nanoneedles, nanotubes, and the role of heteroatom replacement are investigated. One of the motivating factors for these studies has been the recent theoretical result on the stability and unique structural and electronic properties of a suggested new family of all-carbon and carbon rich nanoneedles.²⁶ However, the unique structural and electronic properties of nitrogen nanostructures differing from that of carbon might indicate that such needlelike and tubular nitrogen nanostructures have peculiar applications as building blocks for nanomaterials and as nanostructure devices, containers for storing gas, and potential ligands in synthetic chemistry.

II. COMPUTATIONAL METHODOLOGY

The geometrical structures and stability of nitrogen nanostructures were determined using the Gaussian 03 program²⁷

with the DFT method at the level of B3LYP/6-31G**.²⁸⁻³⁰ For the verification and characterization of energy minima and transition structures ("transition states"), harmonic vibrational frequency calculations were performed at the same level of theory. The binding energies (E_B) are calculated with respect to ground-state atoms present in the molecule, considering for instance the following formal reaction: $N_xH_y \rightarrow xN + yH$, $E_B = E_{N_xH_y} - (xE_N + yE_H)$. Band gaps are calculated with reference to the difference $E_{LUMO} - E_{HOMO}$. The electron density distributions and the shapes of the electron density clouds in both the bonding regions and the peripheral regions of these nanostructures were analyzed in order to elucidate some of the unusual, but essential features of the bonding patterns. For stability studies, minimum energy path calculations³¹ were performed starting at the transition state structures with a coordinate stepsize of 0.1 (amu)^{1/2} bohr.

III. RESULT AND DISCUSSIONS

3.1. Optimum Geometrical Structures and Their Stabilities. Nitrogen nanoneedles and nanotubes formed by units of N_{2m} ($m = 2-6$) and terminated by hydrogen atoms are depicted in Figure 1. The stable geometries of poly- N_4 (2-6 unit layers, D_{2h}), poly- N_6 (2-10 unit layers with different

conformations for the terminating H atoms, D_{3h}), poly- N_8 (2–6 unit layers, D_{4h}), poly- N_{10} (2 and 3 unit layers, D_{5h}), and poly- N_{12} (2 unit layers, D_{6h} , D_{2h} , and D_2) were optimized at the level of B3LYP/6-31G** and characterized to be minima with all real vibrational frequencies. These results indicate no apparent difficulties for forming very long “infinite-length” NNNs or NNTs by units of N_{2m} ($m = 2-5$).

However, some of the actual structures become rather complex after $m \geq 6$. Poly- N_{12} (D_{6h}) is not a minimum at all with three imaginary frequencies. When the symmetry of poly- N_{12} was reduced to D_{2h} , a saddle point was found. On the other hand, poly- N_{12} with D_2 symmetry is an energy minimum. The top view of the best geometrical structure of N_{12} is far from maximally symmetric; it tends to deform to a structure with a cross-section of a dumbbell. Evidently, these nitrogen nanostructures differ from carbon nanostructures in a major way. When compared to the geometrical parameters of three-layer nitrogen nanostructures, if the size m of the unit layer N_{2m} increases, then the bond lengths (all close to the N–N single bond length 1.46 Å) within the rings of the middle layers show no large changes except in some of the tighter nitrogen needles of poly- N_4 and poly- N_6 (> 1.50 Å).

Although this has little apparent significance for long tubes and needles, for the actual shorter structures studied, the geometrical arrangements of the terminating groups (for example, the orientation of H atoms) have a strong effect on the molecular total energies. For instance, the energy of three-layer poly- N_6 with H atoms on the side (roughly perpendicular to the molecular axes) is 51.45 kcal/mol lower than that of three-layer poly- N_6 with H atoms on top and bottom (with bonds roughly aligned with the molecular axes). This preference is even more striking for poly- N_8 and poly- N_{10} , where there is no stable conformation having H atoms on top and bottom. Apparently, at the H-bearing terminal N-atoms, the strong preference of lone pairs to align with the molecular axes dominates.

In general, nitrogen compounds containing single and double bonds release substantial amounts of energy when they dissociate into N_2 molecules. For the actual neutral nitrogen nanostructures studied, most bond lengths are similar to or longer than the N–N single bond. Consequently, these molecules have high energies but low stability. Therefore, the question of how to change the environment of these nitrogen nanostructures in order to stabilize them becomes particularly relevant.

When some positive charge is located on the nitrogen clusters, for instance as illustrated by the optimized geometrical parameters of poly- N_6^{4+} (three-layer units), then the N–N bond-lengths all become shorter (Figure 2) than those of the neutral molecule. The calculations on the two layers poly- N_4^{4+} , poly- N_6^{4+} , and poly- N_8^{2+} indicate that these ions have stable energy minima with shorter bonds than those of analogous neutral structures. Figure 3 shows the distribution of electron densities of $H_3(N_6)_3H_3^{4+}$ and $H_3(N_6)_3H_3$. When considering the molecular isodensity contours (MIDCOs) at the isovalue 0.26 au of electron density, then the bonds of the ion still can be seen, but those of the neutral structure appear disrupted at this density level. Consequently, the global depletion of electron density could stabilize these nitrogen clusters by vacating some orbitals with approximate π^* character, allowing these bonds to have more π character

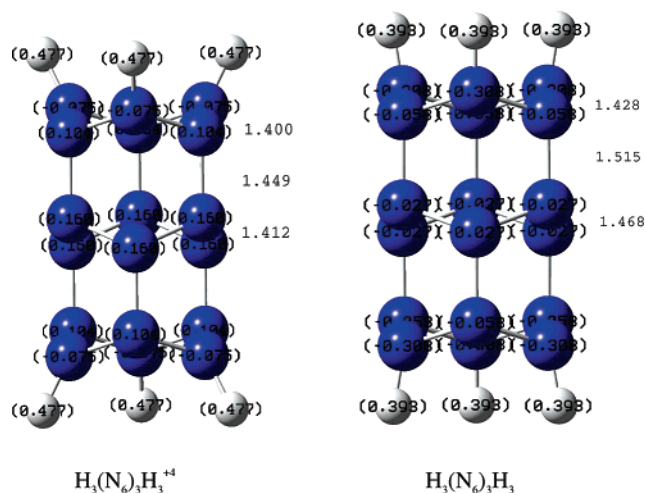


Figure 2. Positive charges increase the stability of nitrogen nanostructures.

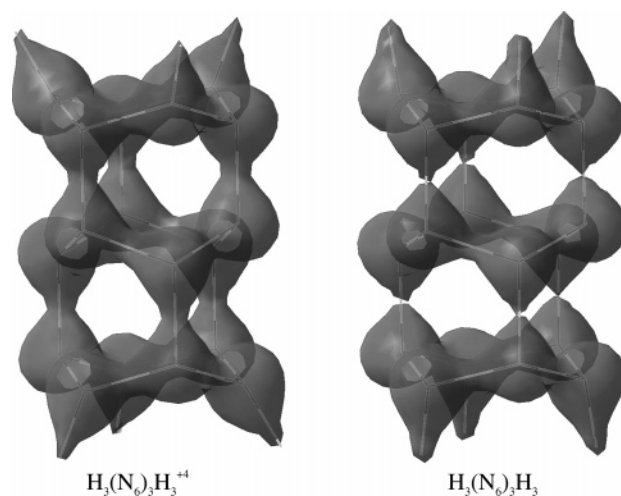


Figure 3. Molecular isodensity contours (MIDCOs) at isovalue 0.26 au.

corresponding to bond orders greater than 1.0, leading to more stable structures. In such a case, the actual charges at various nitrogen atoms and the interactions between charged ions will become an important consideration; the introduction of charges could complicate the synthetic problem considerably. Note, however, that stable charged clusters may also appear as good candidates for HEDMs when they combine with appropriate counterions. Properties of such HEDMs will depend critically on the total charge of a cluster.

Nitrogen clusters are of significant interest as high-energy density materials (HEDMs) for propulsion and explosive applications. Besides high-energy content, the critical properties for effective HEDM molecules are a high dissociation energy barrier and reasonably facile syntheses.

Nitrogen nanoneedles or nanotubes are very different from analogous carbon nanostructures studied already,²⁶ not only in terms of their shape but also in their stability. We know that the neutral molecules are less stable than cationic structures. The bond lengths in the middle layer of three-layer nitrogen nanostructures are the longest. In this paper, two examples of the barriers of dissociation reactions are studied, and the transition state (TS) structures of $H_4(N_8)_3H_4$ and $NO_3(N_6)_3NO_3$ (three-layer nitrogen nanoneedle capped by NO_3) are depicted in Figure 4, showing geometries not very

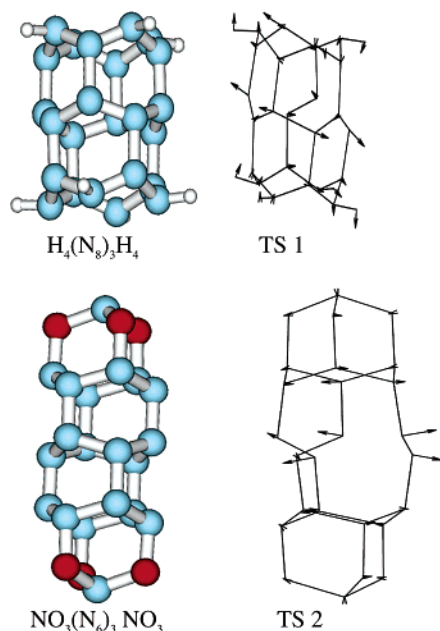


Figure 4. $H_4(N_8)_3H_4$, $NO_3(N_6)_3NO_3$, and the corresponding transition state structures showing displacement vectors of dissociation.

different from those of the energy minima. The vibrational frequencies of these two TS structures and the vectors of dissociation have been determined. For the molecule terminated by NO_3 , the barrier of a “within ring” dissociation of the middle layer is 0.903 kcal/mol corrected by zero point energy at the B3LYP/6-31G** level. This is a very low value, insufficient for stability unless some additional measures are taken. For the molecule terminated by H atoms, the barrier is 7.0 kcal/mol for the “within ring” dissociation of the middle layers, but this barrier is still not high enough to ensure sufficient stability. Thus, discovering new means to increase stability is still one of the main goals of research on this family of nitrogen nanostructures. The development of special local environments for stabilizing nitrogen nanostructures and the search for means for increasing dissociation barriers for all types of nitrogen clusters will be investigated in a forthcoming study.

3.2. The Role of Terminating Groups for N Nanostructures. The terminating groups of these nitrogen nanostructures were investigated in some detail. Poly- N_6 terminated by H, F, NO_3 , N, and P atoms as well as by metal atoms Sc, As, and Bi are optimized and characterized as proper energy minima, with all real vibrational frequencies. The common patterns of optimized geometries are depicted in Figure 5, and the N–N bond lengths in the various layers are listed in Table 1. There are only minor differences among structures with different ending groups, and there is no significant increase of double bond character in any of the examples. Apparently, terminating groups have no large effect on the inherent stability of these structures.

The band gaps of n unit layers of poly- N_{2m} ($m = 2-4$) structures terminated by H atoms or NO_3 are presented in Figure 6. Two main trends are evident: (i) the band gaps decrease as the lengths of the columns increase and (ii) the band gaps increase with the increase of m .

The band gaps of n -layer poly- N_6 structures terminated by various groups are presented in Figure 7. The band gaps are higher (over 3.0–6.0 eV) for poly- N_6 terminated by

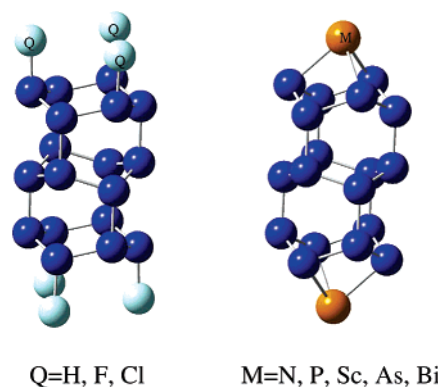


Figure 5. General patterns of optimum geometries of three-layer poly- N_6 structures terminated by H, F, NO_3 , N, P, Sc, As, and Bi.

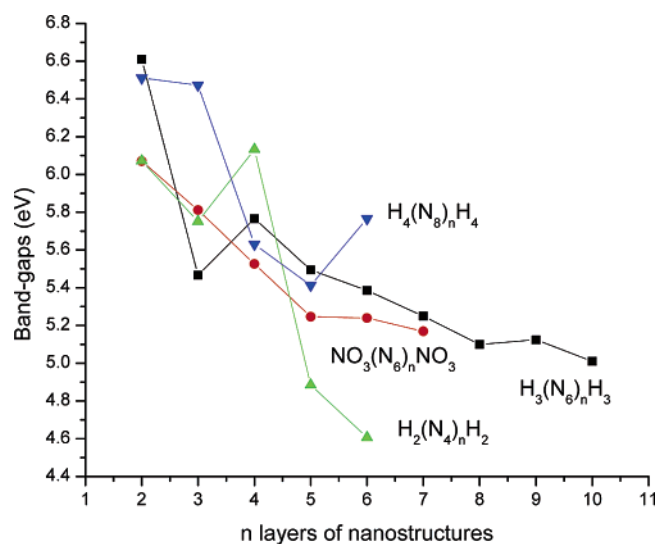


Figure 6. Band gaps of poly- N_{2m} ($m = 2-4$) structures.

Table 1. N–N Bond Lengths of n -Layer Poly- N_6 Structures Terminated by H, F, NO_3 , N, P, Sc, As, and Bi

| n | H | F | NO_3 | N | P | Sc | As ^a | Bi ^a |
|-----|------|------|--------|------|------|------|-----------------|-----------------|
| 2 | 1.42 | 1.46 | 1.460 | 1.49 | 1.48 | 1.48 | 1.55 | 1.54 |
| | 1.54 | 1.52 | 1.498 | 1.47 | 1.47 | 1.51 | 1.51 | 1.52 |
| 3 | 1.42 | 1.45 | 1.463 | 1.49 | 1.48 | 1.49 | 1.48 | |
| | 1.51 | 1.51 | 1.494 | 1.47 | 1.48 | 1.50 | 1.48 | |
| 6 | 1.46 | 1.46 | 1.454 | 1.45 | 1.45 | 1.45 | 1.45 | |
| | 1.42 | | 1.463 | 1.49 | 1.48 | 1.48 | | |
| 7 | 1.52 | | 1.494 | 1.47 | 1.48 | 1.50 | | |
| | 1.46 | | 1.495 | 1.45 | 1.45 | 1.45 | | |
| 7 | 1.49 | | 1.491 | 1.49 | 1.49 | 1.49 | | |
| | 1.46 | | 1.463 | 1.46 | 1.46 | 1.46 | | |
| 7 | 1.49 | | 1.491 | 1.49 | 1.49 | 1.49 | | |
| | 1.42 | | 1.463 | 1.49 | 1.48 | 1.48 | | |
| 7 | 1.52 | | 1.494 | 1.47 | 1.49 | 1.50 | | |
| | 1.46 | | 1.459 | 1.45 | 1.45 | 1.45 | | |
| 7 | 1.49 | | 1.491 | 1.49 | 1.49 | 1.49 | | |
| | 1.46 | | 1.464 | 1.46 | 1.46 | 1.46 | | |
| 7 | 1.49 | | 1.491 | 1.49 | 1.49 | 1.49 | | |
| | 1.46 | | 1.461 | 1.46 | 1.46 | 1.46 | | |

^a With Lanl2DZ, others are with 6-31G**.

nonmetal groups but are lower for those terminated by metal groups (e.g.: below 2.2 eV for Sc ending group). The distribution of electron density changed on these nitrogen nanostructures depending on whether they are terminated by nonmetal or metal atoms. For the charged environment, the band-gap of three-layer poly- N_6^{4+} is 2.23 eV but that of the

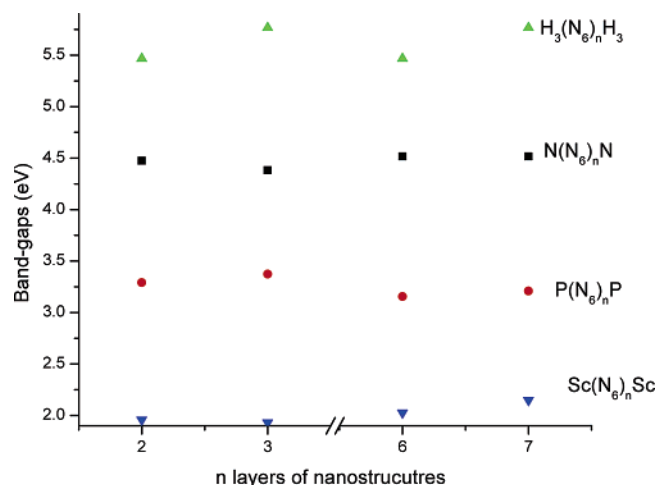


Figure 7. Band gaps of n -layer poly- N_6 structures terminated by various groups.

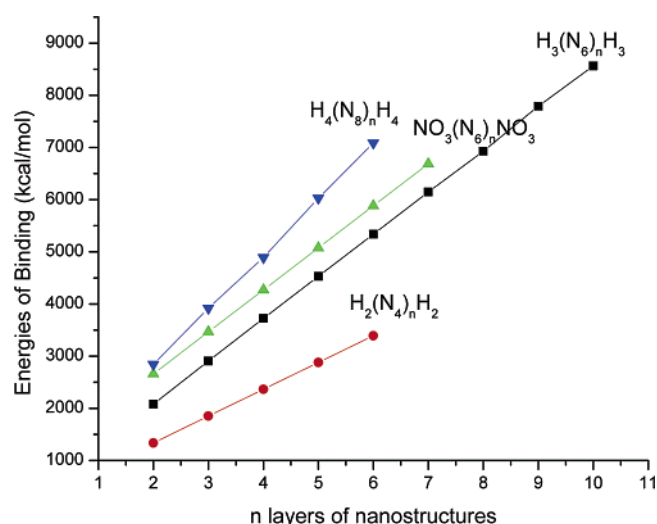


Figure 8. Binding energies of n -layer poly- N_4 , N_6 , and N_8 structures.

neutral structure is high: 5.96 eV. The band gap of two-layer poly- N_4^{4+} is 3.64 eV but that of the neutral structure is higher: 6.36 eV. Thus, the poly- N_6 structure in a suitably charged environment may exist and function as a HEDM, and it might also have some special electronic properties. Band gaps can be affected greatly by a variable charge of the environment, for example, the metallic character could be increased. Such a nitrogen nanostructure might have tunable electronic properties relative to a change in charge environment.

3.3. The Binding Energies of Nitrogen Nanostructures. Figure 8 shows the binding energies of n -layer nanostructures. In this work, we have studied the structures of $H_3-(N_6)_nH_3$ ($n = 2-10$), and based on the calculated optimum geometrical parameters and associated vibrational frequencies of these molecules, these structures were proved to be proper energy minima. The curves of binding energies E_b shown

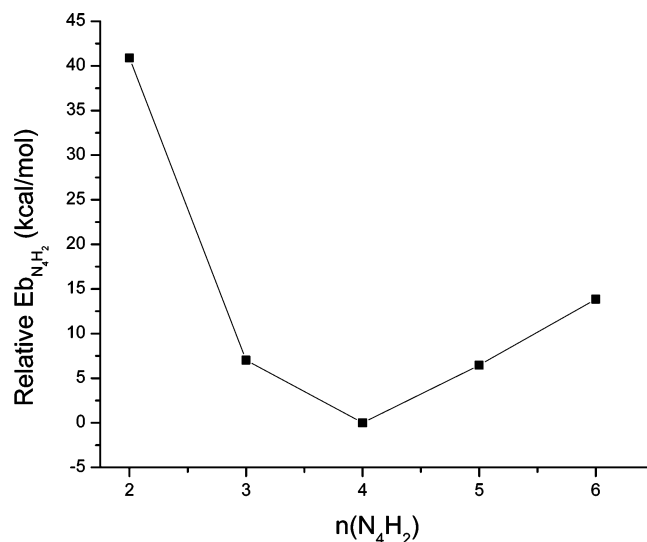


Figure 9. The relative binding energies per N_4H_2 of two layers of poly- N_{2m} ($m = 2-6$) structures.

for the poly- N_6 structures with different ending groups all are nearly parallel straight lines, that is, the bond types show no change with increasing n . If one considers layer units of a given type, then the energy of binding increases with m of the poly- N_{2m} structures. Although we have actually calculated structures and electronic properties of NNS only up to 10 layers, from the tendency of the gradient of E_b , which is nearly constant with increasing m for each different terminal group and diameter size, we nevertheless conclude that the bond forming tendency does not change much with length, and extended (“infinite-length”) nitrogen nanostructures are likely to exist.

Whereas in Table 2 and Figure 9, the evidence is limited to the actual molecules studied, the optimized geometries suggest that the size of the single-ring unit layer of nitrogen nanostructures could not increase limitlessly. The binding energy of N_4H_2 in poly- N_8 is the lowest one and increases with m . Poly- N_8 is likely to have the largest diameter single-ring unit layer of nitrogen nanostructures with D_{mh} symmetry. Poly- N_{12} prefers D_2 symmetry to D_{6h} symmetry. This is also consistent with the results of geometry optimizations since there is no evidence for an apparent nitrogen “graphite” structure, and nitrogen atoms prefer to form smaller rings.

3.4. Composite Nanostructures: Nitrogen Nanobundles with Carbon Backbone. After the theoretical structures and stabilities of nitrogen “nanoneedles” and “nanotubes” have been determined, it was natural to test whether such nitrogen nanostructures can possibly combine to form nitrogen nanobundles (NNBs), with the help of some carbon atoms serving as connections between the individual nitrogen nanostructures.

The top and bottom terminal units of three unit types of nitrogen composite nanobundles, a , b , and c , terminated by H atoms are shown in the first row of Figure 10; the middle units of nanobundles related structures a , b , and c are shown in the second row as structures d , e , and f , respectively. These

Table 2. Binding Energies per N_4H_2 of Two-Layer Poly- N_{2m} ($m = 2-6$) Structures

| unit | N_4 | N_6 | N_8 | N_{10} | N_{12} |
|------------------------------|----------------|----------------|----------------|----------------|----------------|
| E (hartree)/ZPE (kcal/mol) | 219.9818/26.40 | 220.0366/26.98 | 220.0492/27.81 | 220.0353/27.57 | 220.0265/27.44 |

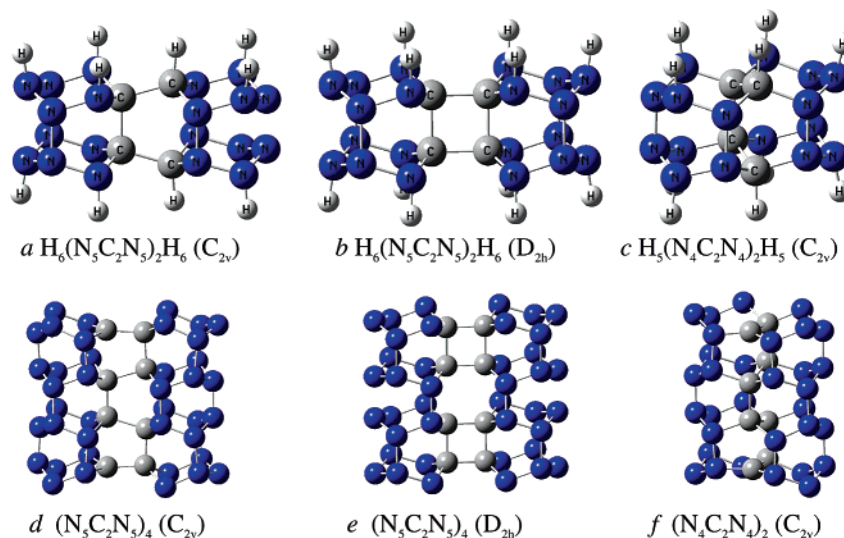


Figure 10. Two-layer nitrogen–carbon nanobundles (*a*, *b*, and *c*) with terminal units only and four-layer intermediate units (*d*, *e*, and *f*) of composite nitrogen–carbon nanobundles.

units of NNBs are fully optimized with all real vibrational frequencies at the level of B3LYP/6-31G**. Units *a* and *b* are isomers with different symmetries: the energy of structure *b* (D_{2h}) is 3.07 kcal/mol lower than that of *a* (C_{2v}). In the middle of these structures, carbon atoms form “bridges” to connect two partially “split” nitrogen nanotubes, reducing the repulsion of the high negative charges of the nitrogen atoms. This is one apparent way to form composite nitrogen-bundles by using a formal backbone of connecting carbon atoms. The fact that these structures are proper energy minima suggests that such composite structures are likely to overcome the problem of low stability of pure N nanostructures. Furthermore, the generation of nanobundles provides a method for the construction of structures with large diameters, which are apparently not favored by pure nitrogen nanostructures.

There are a large number of potential nanostructures involving the principle of combining nitrogen and carbon. A detailed study on such structures, the determination of theoretical standard heats of formation, and the analysis of kinetic stability by dissociation barrier will be investigated in a forthcoming study.

IV. SUMMARY

We conclude that extended (“infinite length”) nitrogen nanoneedles and nanotubes can be formed theoretically but apparently only with rather limited diameter. However, by involving carbon atoms as bridge for combining nitrogen nanotubes and nanoneedles into “composite” nanobundles, the diameter can effectively be increased. Charge depletion can stabilize even fairly complex nitrogen nanostructures. Nitrogen nanotubes and nanoneedles might have tunable electronic properties with respect to modulation of the local charge environment.

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