Laterally Extended Spiral Graphite Analogue Boron−Nitrogen Helices

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Ab initio self-consistent field molecular orbital and density functional theory calculations have been performed on a series of extended helical boron−nitrogen analogues of a "spiral graphite", the [*N*]polymethylenylnaphthalenes ($N = 6$, 8, and 12), with the molecular formula $N_xB_yH_z$ (where $x = 28$, 37, and 55, $y = 27$, 36, and 54, $z = 23$, 29, and 41). Interchanging the positions of the boron and nitrogen atoms in the helix leads to very similar structures $N_{x-1}B_{y+1}H_z$ in all three studied cases. The electronic structure and the optimum geometries of these helices were investigated at the HF/6-31G(d,p) and B3LYP/6-31G(d,p) levels of theory. Electron density contours were calculated for the largest helices at the B3LYP/6-31G(d,p) level of theory.

I. Introduction

Boron−nitrogen compounds have been studied from many perspectives; for example, borazine based polymers have been considered as precursors for the synthesis of boron−nitride ceramics.[1,2] An early theoretical study[3] investigated molecules containing up to three fused borazine rings, predicting boron−nitrogen polymers containing a larger number of six-membered rings. Further studies reported also on the stability of cycled-fused borazines,[4] beltlike structures, analogues of the carbon based cyclacenes, and the boron−nitrogen analogues of acenes,[5] structures comprised of linearly fused borazine rings.

In earlier studies, our group investigated[6,7] the structure, energy, and relative stability of hydrogenated boron−nitrogen analogues of angular fused-ring structures, like helicenes, phenylenes, and single-turn polymethylenylnaphthalenes and nonhydrogenated boron−nitrogen analogues of helicenes, respectively.

Based on the quoted studies, in this work, computational investigations on a series of laterally extended boron−nitrogen helices are being reported. Their carbon analogues were studied recently,[8] at the HF/6-31G(d) level of theory; the fundamental pattern of these structures was considered a "model toward helical graphites". The single-turn boron−nitrogen analogue of polymethylenylnaphthalene, comprised of six fused units, was briefly discussed in one of our recent studies,[6] where a large energy difference has been reported between the two possible structures. Some of these structures are derivable from one another by interchanging N and B atoms, and structurally they are very similar. One finds isomerism within this family; nevertheless, in some cases they are not necessarily strictly isomeric structures. As seen in ref 6, for strict isomerism, an even number of heavy atoms is required in the fused borazine rings or hexagonal type units generated by the alternation of the positions of the boron and nitrogen atoms. In the case of the boron−nitrogen analogues of polymethylenylnaphthalenes, this condition is not generally fulfilled; nevertheless, interchanging N and B atoms leads to some interesting structures discussed in the following sections of the present paper.

Some of these structures are likely to serve as building blocks in the synthesis of novel springlike helical boron−nitride compounds, with applications in nanotechnology, especially if flexible interconnecting building units between geometrically distant functional units are needed.

II. Computational Methodology

Geometry optimization calculations were performed for the boron−nitrogen analogues of [*N*]polymethylenylnaphthalene ($N = 6$, 8, and 12) at the Hartree−Fock and DFT levels of theory using the B3LYP hybrid functional[9,10] with the use of the 6-31G(d,p)[11,12] basis set as implemented in the Gaussian 03 software package.[13] Vibrational frequencies were computed by determining the second derivatives of the energy for all optimized geometries at the same levels of theory, in order to verify the energy minima. Raman intensities, which demand large amounts of computational resources, were not computed.

III. Results and Discussion

Geometries of the optimized structures of the boron−nitrogen analogues of [*N*]polymethylenylnaphthalene ($N = 6$, 8, and 12) are depicted in Figure 1. An interesting aspect of these helices is that the alternation of the positions of the boron and the nitrogen atoms leads to very similar helical conformations (see structures **1**−**6** in Figure 1). Even though in both structures the number of existing bonds and the number of atoms are the same, the total number of heavy atoms is odd; hence, one of the helices has an extra nitrogen atom, and the other has an extra boron atom.

From now on we will refer to these structures as $N_xB_yH_z$ helix (**1**, **3**, and **5**) and $N_{x-1}B_{y+1}H_z$ helix (**2**, **4**, and **6**), where *x* represent the number of nitrogen, *y* the number of boron, and *z* the number of hydrogen atoms, respectively.

Investigations on all the optimized helices **1**−**6** confirmed the existence of energy minima by having real vibrational frequencies at both levels of theory. The lowest vibrational frequencies correspond to springlike motions, observed also in helical systems studied earlier,[6,7] a potentially useful aspect in nanotechnology. Marked with *a*, *b*, *c*, *d*, *e*, *f*, and *g* in

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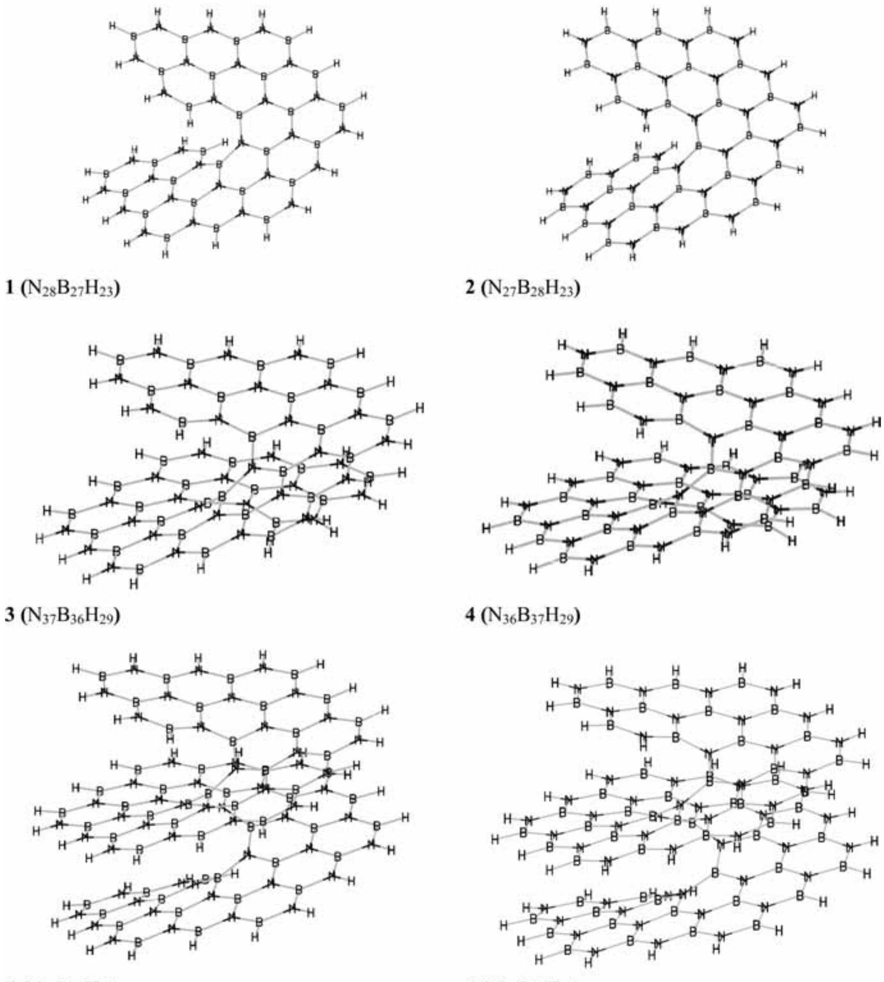


1 ($N_{28}B_{27}H_{23}$)

2 ($N_{27}B_{28}H_{23}$)

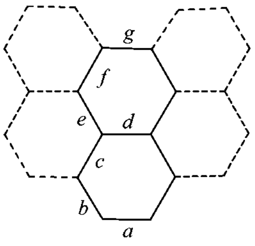
3 ($N_{37}B_{36}H_{29}$)

4 ($N_{36}B_{37}H_{29}$)

5 ($N_{55}B_{54}H_{41}$)

6 ($N_{54}B_{55}H_{41}$)

Figure 1. Optimized geometries of boron−nitrogen helices **1**−**6**.



helix	Bond type *a*	Bond type *g*
1	1.418 - 1.419 (1.422 - 1.423)	1.454 - 1.455 (1.458 - 1.459)
2	1.418 - 1.419 (1.422)	1.456 - 1.457 (1.461 - 1.463)
3	1.418 - 1.419 (1.422 - 1.423)	1.453 - 1.457 (1.457- 1.461)
4	1.418 - 1.419 (1.421 - 1.423)	1.452 - 1.460 (1.457- 1.465)
5	1.418 - 1.419 (1.423 - 1.424)	1.455 - 1.458 (1.459 - 1.462)
6	1.418 - 1.420 (1.422 - 1.424)	1.453 - 1.460 (1.456 - 1.465)

Figure 2. Bond lengths (in angstroms) at the HF and DFT (in parentheses) levels of theory for bond types *a* and *g* in the optimized boron−nitrogen helices **1**−**6**.

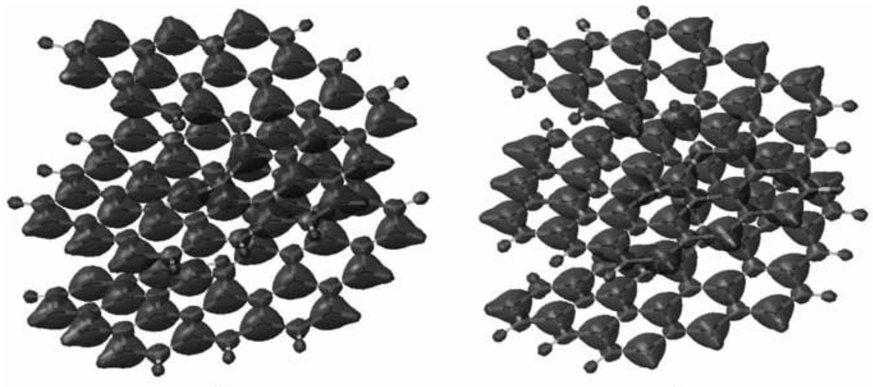


Figure 3. Electron density isocountours of boron−nitrogen helices **5** and **6** at 0.20 au.

TABLE 1: Calculated Energies (in Hartrees) of the Boron−Nitrogen Helices 1−6

molecule	level of theory	
	HF/6-31G(d,p)	B3LYP/6-31G(d,p)
1, $N_{28}B_{27}H_{23}$	−2207.69	−2220.95
2, $N_{27}B_{28}H_{23}$	−2177.90	−2191.02
3, $N_{37}B_{36}H_{29}$	−2924.48	−2942.02
4, $N_{36}B_{37}H_{29}$	−2894.69	−2912.09
5, $N_{55}B_{54}H_{41}$	−4358.06	−4384.16
6, $N_{54}B_{55}H_{41}$	−4328.27	−4354.23

Figure 2 are the calculated bond lengths of the boron−nitrogen helices. The areas at the peripheries of the helices characterized by bond type *a* resemble partial aminoborane fragments. In these cases bond type *a* has a pronounced double-bond character (1.418−1.419 Å), close to the value in the real aminoborane[14] (1.400 Å).

Bond type *g* is connecting trivalent boron and nitrogen atoms in the inner part of the helices; it is weaker in strength when compared to bond type *a* and can have a determining factor in the curvature of the helices. As seen in Figure 2, the range, as well as the maximum value of the length of bond type *g*, increases slightly going from the simple helices **1** and **2** to the larger helices **5** and **6**, whereas the length of bond type *a* remains almost constant throughout the series at both levels of theory.

The values of the lengths of the remaining bond types *b*, *c*, *d*, *e*, and *f* are less systematic; they fall between 1.429 annd 1.452 Å at the HF and 1.433 and 1.457 Å at the density functional levels of theory. The bonding pattern appears to be stable and equilibrated, in agreement with the results of electron density calculations, as seen in the calculated shapes of density isocontours at 0.20 au, presented in Figure 3.

From an energetic point of view, the differences between the two types of extended helices are drastic (Table 1). In all three cases, the structures containing more nitrogen atoms are lower in energy than their counterparts having more boron atoms. The difference in energy between the two types of helices is around 30 hartree, which is consistent with the energy difference between the boron and the nitrogen atom. Nevertheless, deviations from the reference difference, as defined by the energy difference between the N and B atoms, provide indications about smaller energetic preferences for such helices. In a future study of additional helical structures, focusing on the special role of lone pairs of the N atoms in peripheral and other locations, this aspect will be the subject of further investigation.

IV. Summary

The electronic structures of novel laterally extended boron−nitrogen analogues of angular [*N*]polymethylenylnaphthalenes (*N* = 6, 8, and 12) were investigated. These structures may serve as potential models for springlike nanostructures, where electronic and energetic stability properties can be influenced by outside interactions with the electron-rich N atoms, especially by lone pair interactions, and alternatively by the electron-poor B atoms. By alternating the positions of the boron and nitrogen atoms, two very similar structures are possible, the $N_xB_yH_z$ helix (**1**, **3**, and **5**) and $N_{x-1}B_{y+1}H_z$ helix (**2**, **4**, and **6**). Between the two type of systems, the $N_xB_yH_z$ and the $N_{x-1}B_{y+1}H_z$ helix, the stabilizing role of a larger number of nitrogen atoms must be considered in the context of also having a large number of possibly reactive lone pairs.

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