J. Phys. Chem. A **2008,** *112,* 2477−2481 **2477**

Theoretical Study on the Structure and Stability of Some Unusual Boron−Nitrogen Helices

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Received: August 27, 2007; In Final Form: November 16, 2007

Ab initio self-consistent field molecular orbital and density functional theory calculations have been performed on a series of helical structures comprised of boron−nitrogen analogues of extended helicenes, with helically arranged N fused benzene rings, and alternating N benzene units fused to $N - 1$ cyclobutadiene rings as reference structures. The electronic structure and stability of boron−nitrogen analogues of angular [N]helicenes, [N]phenylenes ($N = 5, 6, 7, 12$), and [N]methylenylnaphthalenes ($N = 6$) were investigated at the HF/6-31G(d) and the B3LYP/6-31G(d) levels of theory. The presence of an even number N of rings in the boron−nitrogen [N]helicenes leads to the possibility of angular isomers. Electron density contours were calculated in order to interpret the existing bonding patterns. These structures may provide supramolecular building blocks and macromolecular "springs" with unusual electronic properties.

I. Introduction

The interest in the structure, bonding, and electronic properties of boron−nitrogen clusters has increased in recent years.[1−4] The boron−nitrogen atom pair, being isoelectronic with the carbon−carbon pair, has been a likely replacement of the latter in a variety of carbon-based compounds. The change in nuclear charges introduces several specific effects in the structure as well as the electronic properties, which provide new options for interesting molecular systems and potential nanomaterials.

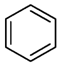
The discovery of hexahelicene[5] encouraged investigations toward helically extended π systems leading, for example, to the synthesis of helical [7]phenylene.[6] These structures are angular systems formed from N fused benzene rings in the case of helicenes and N fused benzene rings with $N - 1$ interposed cyclobutadiene rings in the case of phenylenes. Additional interest is generated by their unusual chirality and optical properties.[7,8] The geometry and energetics of phenylenes, helicenes, and their isomers has been the subject of numerous theoretical studies.[9−12] Most recently,[13] theoretical investigations were carried out on the stability of more extended systems, up to double-turn polyhelicenes, polyphenylenes, and analogous structures, as potential precursors toward helical graphites.

The pairs B−N and C−C are similar in size, but while the bonding involved between the carbon atoms is symmetrical, the B−N bond is an asymmetric one, which results in novel structural features and electronic properties.

Borazine,[14] the boron−nitrogen analogue of benzene is well-known. Borazanaphthalene, the boron−nitrogen analogue of naphthalene, first observed as a product formed during the gas-phase pyrolysis of borazine,[15] is also characterized both experimentally[16−18] and theoretically.[19] An earlier study investigated molecules containing three fused borazine rings,[20] predicting a possibility for the existence of boron−nitrogen polymers containing larger number of rings. Further studies reported on the stability of cycled fused borazines,[21] which are beltlike structures analogues of the carbon based cyclacenes. A series of linearly annelated boron−nitrogen analogues of acenes were also the subjects of detailed density functional calculations.[22] Most recently,[23] the synthesis of a tubular conical BN helix structure, having elastic properties has been reported. Helical all-nitrogen and helical nitrogen-rich fused-ring clusters were studied as well;[24] however, to our knowledge boron−nitrogen analogues of the helicenic and phenylenic angular systems are not yet the subjects of any detailed theoretical study.

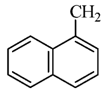
In the present paper computational investigations are reported for a series of single- and double-turn boron−nitrogen analogues of [N]helicenes and their angular isomers (possible only if N is an even number), [N]phenylenes, and [N]methylenylnaphthalenes. The boron−nitrogen analogues of benzene (**a**), cyclobutadiene (**b**), and methylenylnaphthalene (**c**) are the structural units of these angular systems. N fused **a** rings form the single-turn ($N = 5, 6, 7$) and double-turn ($N = 12$) versions of the boron−nitrogen analogues of [N]helicenes. An even number N of rings in the boron−nitrogen helicenes leads to the existence of angular isomers, which can be distinguished by the different arrangements of the B and N atoms in the terminal ring (Figure 1). For brevity, in this paper the **d** isomer will be denoted as **BN** and the **e** isomer as **NB**.

a



b

c



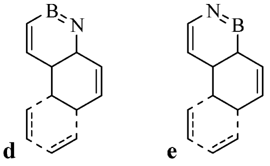


Figure 1. The two possible structures **d** and **e** in the case of helicenes with even N rings, where the B and N atoms, one of them present at each vertex of these structural formulas, are shown only along one bond.

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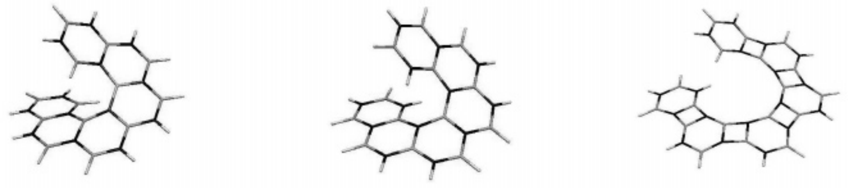
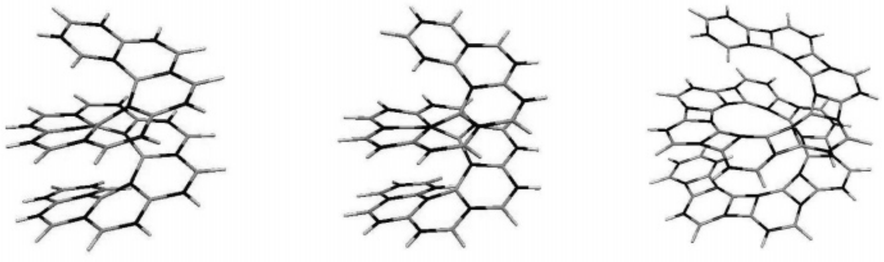
10.1021/jp076844n CCC: $40.75

(1) BN[5]helicene **(2)** BN[5]phenylene



(3a) NB[6]helicene **(3b)** BN[6]helicene **(4)** BN[6]phenylene

(5) BN[7]helicene **(6)** BN[7]phenylene



(7a) NB[12]helicene **(7b)** BN[12]helicene **(8)** BN[12]phenylene

Figure 2. The geometries of boron−nitrogen analogues of [*N*]helicenes and [*N*]phenylenes.

The boron−nitrogen analogues of [*N*]phenylenes are comprised of *N* ($N = 5$, 6, 7, and 13) alternating **a** units fused to $N - 1$ **b** units. Finally the helical boron−nitrogen analogue of [*N*]polymethylenylnaphthalene is obtained with *N* fused **c** units.

II. Computational Methodology

The structures **1**−**8** (Figure 2) were optimized at two different levels of theory, Hartree−Fock and density functional theory (DFT) with the B3LYP functional, using the 6-31G(d) basis set.[25,26] All these methods are implemented in the Gaussian 03 software package.[27] For all optimized geometries, harmonic vibrational frequencies were computed at the same level of theory. The lowest vibrational frequencies for all the optimized structures, no imaginary frequencies among them, are shown in Table 1. In order to investigate the bonding pattern in the systems, electron density analysis was performed at the HF/6-31G(d) level. The levels of theory and basis sets used in the present study do not account for the presence of London dispersion forces. Although these forces may have an increased role in larger systems, their study was not the primary goal of this investigation. To address this problem, a more comprehensive future study is needed.

TABLE 1: The Lowest Vibrational Frequencies (cm^{-1}) of the Studied Boron−Nitrogen Helices. (Calculated Frequency Values at HF/6-31G(d) Shown in the First Column, Followed by Those at B3LYP/6-31G(d) in the Second Column)

BN[5]helicene, **1**	47.1872	45.5776
BN[6]helicene, **3a**	34.2722	31.9657
NB[6]helicene, **3b**	31.9367	32.4448
BN[7]helicene, **5**	32.0089	26.7656
BN[12]helicene, **7a**	39.1514	34.4146
NB[12]helicene, **7b**	37.5130	36.5825
BN[5]phenylene, **2**	18.1709	19.6884
BN[6]phenylene, **4**	19.5756	16.4399
BN[7]phenylene, **6**	14.7192	12.6586
BN[13]phenylene, **8**	13.3656	11.5141
BN[6]methylenylnaphthalene, **9a**	15.8761	15.4080
NB[6]methylenylnaphthalene, **9b**	16.6391	13.0773

III. Results and Discussions

Geometries of the optimized structures are presented in Figure 2, and the bond lengths in the single-turn boron−nitrogen helices are indicated in Figure 3.

Investigations on the optimized structures of **(1)**, **(3a)**, **(3b)**, **(5)**, **(7a)**, and **(7b)**, the boron−nitrogen analogues of [*N*]-helicenes ($N = 5$, 6, 7, 12), confirmed the existence of energy minima by having real vibrational frequencies at both the Hartree−Fock and DFT levels with the 6-31G(d) basis set.

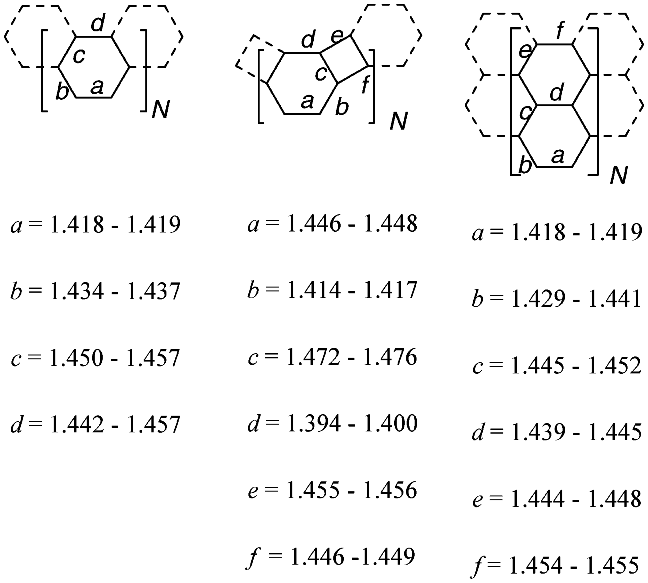


Figure 3. Geometries and bond lengths (in angstroms) of single-turn boron−nitrogen fused-ring helices at HF/6-31G(d).

Noted with *a*, *b*, *c*, and *d* in Figure 3 are the bond lengths of the boron−nitrogen analogue of helicenes found for the non-terminal rings of the helical systems. These bonds appear longer than those in their reported carbon analogues,[13] which could result from the weakening of the π bonding in the boron−nitrogen ring due to the electronegativity difference between the boron and the nitrogen atoms.

However, these distances still fall in the range of the experimentally determined bond length values (1.400−1.453 Å) of borazanaphtalene,[18] which could be considered a simple model somewhat similar to these fused helical systems. The bonding pattern appears to be stable and nearly uniform with stronger bonds on the peripheries of the rings (bond type *a* in Figure 3) that are justified by general electron repulsion effects: electrons seek the periphery of extended structures, allowing them to increase their formal "mutual distances". This is in agreement with the results of more detailed electron density shape analysis of these molecules (Figure 4). The isocontours at the high-density value 0.30 e^-/bohr^3 already show significant deformations from local spherical shape of the constituent atoms. At the isocontour value of 0.20 e^-/bohr^3, the electron density analysis confirms bond type *a* being the strongest. The 0.12 e^-/bohr^3 electron density contours are special. On the one hand, they show a level of electron density where a single, but multiply connected, contour presents a prominent alteration of electron rich and electron deficient atoms. On the other hand, one can notice a rare phenomenon: actual hexagonal local structures give rise to nearly perfect triangular holes, a feature that may be useful in "shape tuning" of local interactions. Interactions occurring at high density are effected by hexagonal patterns, while low-density interactions are effected by triangular patterns.

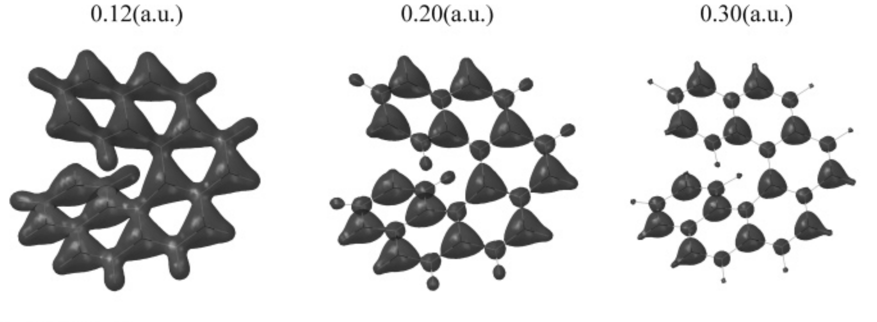
TABLE 2: Total Energies (hartrees) of Boron−Nitrogen Analogues of [*N*]Helicenes

	level/basis set	
molecule	HF/6-31G(d)	B3LYP/6-31G(d)
BN[5]helicene, **1**	−879.7494	−885.1388
BN[6]helicene, **3a**	−1039.3953 (3.5)[a]	−1045.7518 (4.1)
NB[6]helicene, **3b**	−1039.4009 (0.0)	−1045.7584 (0.0)
BN[7]helicene, **5**	−1199.0472	−1206.3717
BN[12]helicene, **7a**	−1997.2850 (4.3)	−2009.4474 (4.8)
NB[12]helicene, **7b**	−1997.2919 (0.0)	−2009.4550 (0.0)

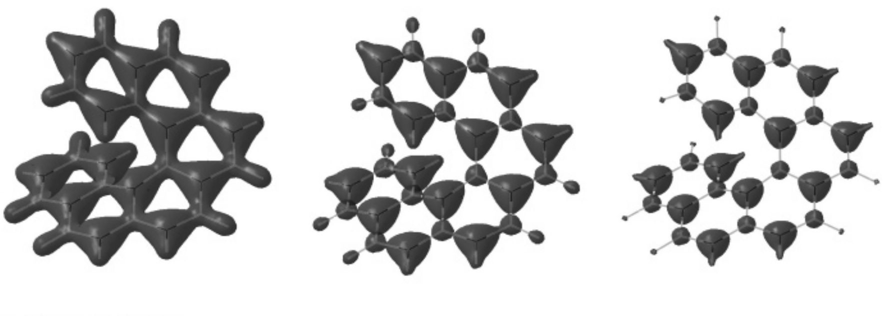
[a] The values in parenthesis show the energy in kcal/mol of the BN isomers, relative to the NB isomers in the case of $N = 6$ and $N = 12$.

Taking into consideration the number of rings, as *N* increases, a decrease in the total energy of unit structures is observed at both levels of theory (Table 2). The gradual energy changes from molecule to molecule are approximately −159.65 and −160.61 ± 0.01 hartrees at the HF/6-31G(d) and the B3LYP/6-31G(d) levels, respectively.

In case of an even number of *N* rings, both in the single (**3**) and double helix (**7**), the NB isomers **(3b)** and **(7b)** are energetically more stable than their BN counterparts. The difference in the relative energy values between the two isomers is 3.5 and 4.1 kcal/mol for a single helix and 4.3 and 4.8 kcal/



(3a) BN[6]helicene



(3b) NB[6]helicene

Figure 4. Electron density isocontours (au. = e-/bohr3) of single-turn boron−nitrogen helicenes.

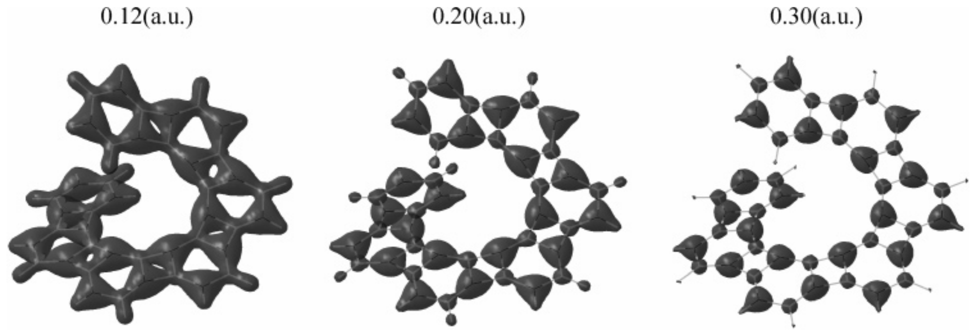
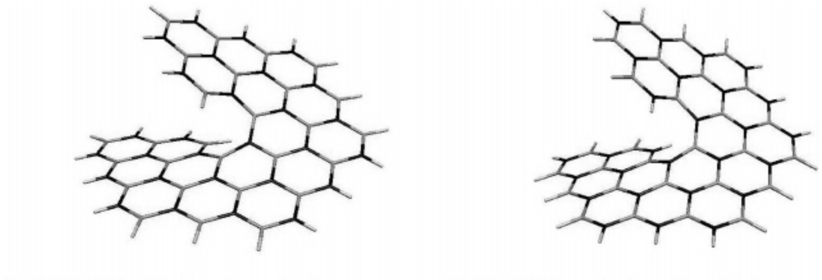
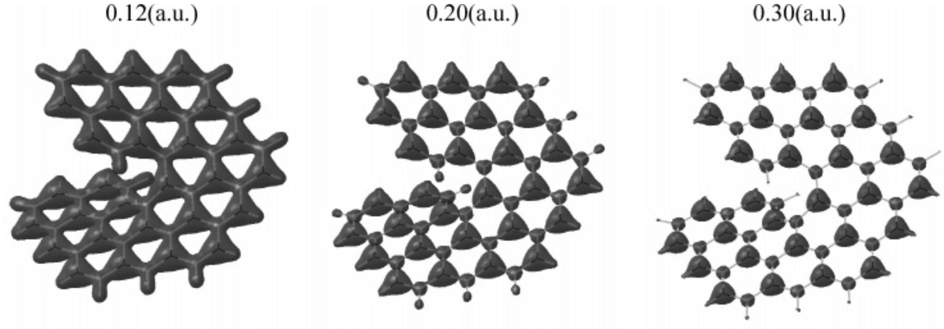


Figure 5. Electron density isocontours (au. = e^-/bohr^3) of single-turn **(6)** BN[7]phenylene.

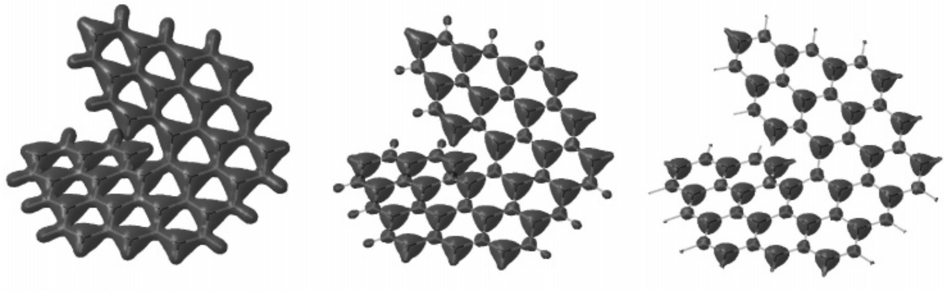


(9a) BN[6]methylenylnapthalene **(9b)** NB[6]methylenylnapthalene

Figure 6. The geometries of double-layered BN and NB helices.



(9a) BN[6]methylenylnapthalene



(9b) NB[6]methylenylnapthalene

Figure 7. Electron density isocontours (au. = e^-/bohr^3) of boron−nitrogen methylenylnaphthalenes.

mol for a double helix, at the HF/6-31G(d) and B3LYP/6-31G-(d) levels, respectively.

The boron−nitrogen analogues of [*N*]phenylenes **(2)**, **(4)**, **(6)**, and (**8)** were also optimized and found to be energy minima structures, confirmed by vibrational frequency calculations. Except for BN[5]phenylene, which has a planar structure, all the others have helical geometries (Figure 2). The unit structures in all species are characterized by six B−N bond lengths, noted with *a*, *b*, *c*, *d*, *e*, and *f* in Figure 3.

In the helices (**4)**, **(6)**, and **(8)**, the bond lengths are ranging from 1.394 to 1.476 Å, where bond types *d*(1.394−1.400 Å) and *b*(1.414−1.417 Å) have a prominent double-bond character, which is close to the experimentally determined B−N double bond length (1.400 Å) in aminoborane.[28]

The alternating strong and weak bonds evidenced also in the electron density at the isocontour value of 0.20 e^-/bohr^3 (Figure 5) are suggesting an approximate "Kekule-like" structure of these systems.

Similarly to the results obtained for the boron−nitrogen helicenes, the energy results (Table 3) show the analogous gradual total energy contributions of unit structures with the increasing number of *N*.

TABLE 3: Total Energies (hartrees) of Boron−Nitrogen Analogues of [*N*]phenylenes

molecule	level/basis set HF/6-31G(d)	B3LYP/6-31G(d)
BN[5]phenylene, **2**	−1196.5797	−1203.8299
BN[6]phenylene, **4**	−1435.4344	−1444.1177
BN[7]phenylene, **6**	−1674.2915	−1684.4076
BN[13]phenylene, **8**	−3107.4371	−3126.1526

TABLE 4: Total Energies (hartrees) of Boron−Nitrogen Analogues of [*N*]methylenylnaphthalenes

molecule	level/basis set HF/6-31G(d)	B3LYP/6-31G(d)
BN[6]methylenylnaphthalene, **9a**	−2207.6266	−2220.8878
NB[6]methylenylnaphthalene, **9b**	−2177.8436	−2190.9700

The values of energy changes are nearly constants, up to five digits, approximately −238.85 and −240.29 ± 0.01 hartrees at the HF/6-31G(d) and the B3LYP/6-31G(d) levels, respectively.

By increasing the number of fused boron−nitrogen rings, double-layered BN **(9a)**, and NB **(9b)** helices can be obtained (Figure 6).

They were also optimized, and it was found that they are stationary points corresponding to real energy minima with real vibrational frequencies at the HF/6-31G(d) and the B3LYP/6-31G(d) levels of theory.

The BN isomer is energetically more stable than the NB counterpart; the energy difference between the two structures is 29.7830 hartrees at HF/6-31G(d) and 29.9178 hartrees at B3LYP/6-31G(d) level, respectively (Table 4). The apparent reason for this energy difference is that a greater number of nitrogen atoms on the peripheries are better accommodating electrons in case of the BN isomer.

The values of the six most characteristic B−N distances in the helices denoted by *a*, *b*, *c*, *d*, *e*, and *f* in Figure 3 are ranging from 1.418 to 1.455 Å. From the electron density shape analysis at the isocontour value of 0.20 e^-/bohr^3 (Figure 7) and from the inspection of the optimized bond length values it seems that the *a*-type B−N bond is slightly stronger at the peripheries. This follows the general trend concerning peripheries pointed out above.

IV. Summary

Some novel boron−nitrogen analogues of angular helicenes, phenylenes, and methylenylnaphthalenes were investigated. Attention was given to their stability, geometry, and energies, as such molecules could provide useful information in the quest for novel boron−nitrogen-based nanomaterials. These structures may serve as somewhat compressible, “springlike” building blocks in supramolecular constructions.

The primary goal of this study was to investigate the structural stability of some boron−nitrogen systems, where the employed electron density analysis provided an efficient way for pointing out the essential features.

In a future study, we intend to use a wider range of electron density analysis methods, including most of the popular bond index approaches, in part for the purpose of establishing their validity in these unusual cases of boron−nitrogen compounds.

Acknowledgment. This study has been supported by the Natural Sciences and Engineering Research Council of Canada, the Scientific Modeling and Simulation Laboratory, and the Advanced Computation and Visualization Center (CVC) of Memorial University of Newfoundland. Additional thanks go to the Atlantic Computational Excellence Network (ACEnet) for computer resources and to Dr. Peter Warburton for discussions.

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