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Structure, Stability, and Bonding of BC_2N: An ab Initio Study

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Tetra-atomic BC_2N, the building block of the mixed carbon and BN clusters, has been studied at the HF, MP2, and CCSD(T) levels using both double- and triple-ζ basis sets with polarization and diffuse functions. In contrast to the parents C_4 and $(BN)_2$, the linear triplet ($^3\Pi$) BCCN is found to be the most stable and the linear−cyclic energy difference is about 28 kcal/mol. In the cyclic structure, isomers with adjacent B and N atoms are more stable, whereas no general trend of atomic combination has been found in the linear isomers. The preferred sequence of atoms in the linear form depends on the cluster size. The nature of bonding and atomization energies of the parent and hybrid molecules are compared and discussed.

Introduction

Ceramics[1] are not limited to oxide compounds. Non-oxide ceramics, such as borides, carbides, nitrides, and silicides, are also known for their high mechanical strength, hardness, and thermal shock stability and wide variation of electrical properties. One commercially important non-oxide ceramic is boron nitride, BN. Boron nitride is isoelectronic with carbon, and like carbon, its properties are highly dependent on the crystalline modification.[2] BN is primarily found in hexagonal h-BN (α-BN) form that resembles graphite, sphalerite-type β-BN (c-BN) forms related to cubic diamond and wurtzite-type γ-BN forms related to hexagonal diamond. The traditional synthetic routes to h-BN and its properties were reviewed by Archer[3] and Meller.[4] Paine and Narula,[5] in their review article, pointed out that boron nitride is a fascinating ceramic with a potentially bright future in advanced materials.

The discovery of carbon nanostructures such as fullerenes[6] and nanotubes[7] has not only triggered scientific interest about their structure, mechanical, and electrical properties, but also stimulated intense experimental and theoretical interest in BN nanostructures. An early theoretical study by Cohen and collaborators[8,9] predicted that a pure BN tube should be stable. Hamilton et al.[10] first produced a turbostatic tubular form of BN with a diameter on the order of a micrometer from amorphous boron nitride. BN nanotubes have recently been synthesized using an arc-discharge method[11−13] and by annealing amorphous boron particles in a hexagonal BN crucible.[14,15] Electronic band structure calculations[8,9] show that BN nanotubes are wide-gap semiconductors with a gap value around 5.5 eV. On the other hand, carbon tubes are either metallic or semiconductors. Interestingly and in sharp contrast to carbon nanotubes, this gap value in BN nanotubes is independent of the radius, helicity, and wall−wall interaction of the tubes.

Although there are strong similarities in the structures of BN and analogous carbon compounds, their physical, chemical, and electrical properties differ significantly. For example, graphite is semi-metallic and an excellent host material whereas h-BN is an insulator with limited intercalation properties. Diamond is the hardest of all materials but it is exceptionally unsuitable for the abrasion of iron materials and is oxidized at 700−900 °C in air, whereas c-BN is much more inert to iron and is stable up to 1600 °C in air despite the fact that it has only half the hardness of diamond. Intermediate properties, such as chemical inertness superior to that of diamond and a hardness greater than that of c-BN, are expected to be found in BCN materials where CC moieties of carbon compounds are partially substituted by BN units. It has also been predicted[8,16−18] that doping of h-BN into the graphite structure would alter its electronic properties.

Hybrids of C, B, and N have been synthesized by different experimental methods, including chemical vapor deposition (CVD),[18−26] precursor pyrolysis,[27−29] metal-catalyzed laser ablation,[30−32] and arc-discharge methods.[33−35] Synthetic methods, structures, and physical and chemical properties of BCN materials were recently reviewed by Itoh[36] and Kawaguchi.[37] Depending on the synthetic methods, starting materials, temperature, and pressure, different structural forms of BCN (e.g., c-BCN, h-BCN, BCN nanotubes, nanofibers, graphite-like onion, solid solution, etc.) can be obtained. The ratio of B to N in these compounds is close to 1, confirming the substitution of BN in a C network in the B_xN_x stoichiometry. Although different carbon concentrations[38] (BC_xN, $x = 0.6-7$) have been observed, the most reliable overall composition in all forms of BCN materials is BC_2N. However, several other compositions are also possible, such as a nitrogen-rich BCN material, which was recently reported.[39] Polo et al.[26] reported that films of BC_2N are basically a chemically mixed B−C−N ternary phase and not a mixture of C and BN phases.

As predicted, various properties of BCN materials are intermediate between carbon and BN compounds. For example, thermal oxidation resistance[40] of c-BC_2N (h-BC_2N) lies between that of diamond (graphite) and c-BN(h-BN). Transition of c-BC_2N to h-BC_2N occurs at 1800 °C, whereas for carbon and BN compounds, the corresponding values are 2000 and ∼1800 °C. Thin films and layered compound BC_2N are semiconductors,[22] whereas their C and BN counterparts are semi-metallic and insulators (or wide gap semiconductors), respectively. The band gap of BCN is predicted[36,37] to be highly dependent on the atomic arrangement and crystallinity. Unfortunately, BCN materials synthesized so far have all been poorly crystalline, less ordered, and had particle sizes are small. Experimental

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information on the atomic arrangements (structures) and bonding of this interesting class of materials is meager.

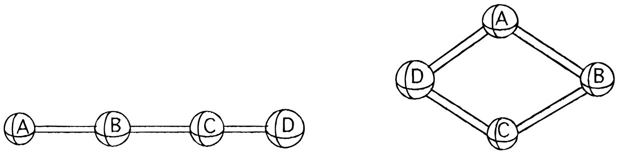
Theoreticians have taken the initiative[41−49] to investigate the electronic structure, bonding, and electrical properties of this interesting class of materials prior to thorough experimental characterization. Cohen and collaborators[41−43] were the first to calculate the electronic structure of BC_2N compounds in the framework of the local density functional formalism. The structural stability of BC_2N has also been studied by Itoh and co-workers[44−47] using an empirical molecular mechanics simulation. Different structural models (eight constituent atoms per unit cell) with different atomic arrangements were considered in those theoretical studies. It has been predicted that the stable structures of BC_2N are formed so as to maximize the number of both C−C and B−N bonds with C−B and C−N bonds disfavored. Atomic arrangements with B−B and N−N bonds are found to be less favorable because of lower bond energies compared to C−C and B−N bonds. It has also been found that a structure with alternate −C−C− and −B−N− chains or rings is the most stable one. Calculations[50] on BC_2N sheets reveal in-plane anisotropic conductivity (in contrast to graphite and BN), and the band gap is highly sensitive to the atomic arrangements and chirality of the tubes. Conversion from graphitic BC_2N to heterodiamond−BC_2N structure has been suggested by Tateyama et al.[47] using a local density approximation. The bond counting rule, i.e., maximum CC and BN bonds, found in layered structures is also found to be valid for heterodiamond−BC_2N. However, there is some experimental (from XPS and ESCA spectra) evidence[22,25,39] for B−C and C−N bonds in BC_2N thin films and in graphite-like forms.

Most prior theoretical studies in this area have serious drawbacks, i.e., geometries are not optimized and stability is determined by means of semiclassical methods in terms of experimental bond energies of the constituent bonds. The importance of this material warrants a more accurate theoretical investigation. In this study, we have considered the tetraatomic system, BC_2N, as the basic building block. For the sake of comparison, isoelectronic C_4 and $(BN)_2$ molecules have also been included in the present investigation. Both isomers of the triatomic BCN molecule, BNC and BCN, have been experimentally characterized,[51] and a high-level ab initio investigation[52] on the structure, stability, and vibrational spectra of BCN has already been reported. We will compare these results with those of tetraatomic BC_2N.

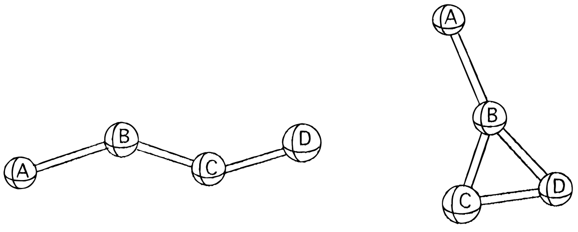
Method of Calculation

All calculations have been carried out using the Gaussian94 package[53] of ab initio codes. Split-valence double-ζ (DZ) quality basis set with polarization functions on all atoms, namely 6-31G*, was used for the initial geomery optimization at HF and MP2 levels. For open-shell cases, UHF and UMP2 methods were used. Only valence electrons were included in the electron correlation evaluation. Vibrational analyses at both levels have been performed to identify the true minimum. To further refine geometries and energetics, MP2(full)/6-311+G(2d) (a triple-ζ (TZ) quality basis set with diffuse and polarized functions on each atom) with all electrons included in the correlation was used following the vibrational analysis at the same level. Since the energies in the UMP2 (for open shell) calculations are generally too high due to spin contamination in the reference UHF wave function, we have used the projected UMP2 (PUMP2) method.[54] Geometry optimizations were also performed at the CCSD(T) (coupled cluster method with all single and double excitations augmented by a quasiperturbative estimate for the effect of triplet excitations) method[55] using the 6-31G* basis set; vibrational analysis was subsequently run at the MP2/6-31G* level. Although the latter frequencies do not strictly apply to a minimum computed at a different level of theory, the results should nonetheless offer a reasonable approximation, particularly since the MP2 and CCSD(T) minima do not differ much.

SCHEME 1



Linear (**I**) Cyclic / Rhombic (**II**)



Trans-bent (**III**) AB(CD) Cyclic (**IV**)

The bonding characteristics of the most stable isomers were examined using bond index analysis[56] and Boys' localized molecular orbitals (LMOs)[57] at the HF level using MP2/6-31G* geometries. The positions of the charge centroids in the molecule are used[58] to identify the bonds (two and three center) and lone pairs (LPs). Atomization energies are evaluated as a difference between the cluster energy and the corresponding atomic energies, without vibrational correction. The first ionization energies (IE) and electron affinities (EA) of the most stable isomers are evaluated using a vertical approximation wherein energies of the ions are calculated at the corresponding geometries of the neutral systems.

Results and Discussion

The different structural forms of BC_2N considered in the present investigation are displayed in Scheme 1. All six possible combinations of atomic arrangements in linear form **I** of BC_2N are considered. For the BN dimer, only BNBN was considered since this combination is found[59,60] to be more stable than other sequences of B and N atoms in the linear form. Since rhombic isomers of C_4 and $(BN)_2$ are energetically competitive with the corresponding linear geometries, cyclic- or rhombic-like forms (**II**) are considered for BNCC and BCNC sequences. As in the linear case, the BNBN combination is the only BN dimer examined. We have also relaxed the restriction of strict linearity and included a possible trans bent structure (**III**) for BC_2N. (It may be noted that the cis bent form is similar to the cyclic or rhombic form and, hence, not considered here.) The other possibility of arranging four atoms is another cyclic form (**IV**) with one atom in the center surrounded by the other three. The AB(CD) notation indicates atom B at the center with C and D completing the ring. Tetrahedral-type structures have been found to relax to the cyclic (**II**) or linear form during geometry optimization.

A. Energetics. The reliability of the methods and basis sets used in this study is first assessed by comparing the results of C_4 with previously reported findings. Among small carbon clusters, the C_4 molecule has received considerable experimental

TABLE 1: Relative Energies^a (kcal/mol) of C_4 Isomers

	II (^1A_g)	**I** ($^3\Sigma_g^-$)	**I** ($^1\Delta_g$)	**II** ($^3B_{3u}$)	**I** ($^3\Sigma_u^+$)
HF/6-31g*	23.69 (0)	0.00 (0)	30.20 (0)	N/A	24.18 (0)
MP2/6-31g*	0.00 (0)	9.81 (0)	24.92 (0)	13.17 (0)	28.22 (0)
MP2(full)/ 6-311+g(2d)	0.00 (0)	4.03 (0)	18.71 (0)	13.55 (0)	22.19 (0)
CCSD(T)/6-31g*	0.00	2.48	10.90	20.67	23.91

[a] Number of imaginary normal vibrational modes in parentheses.

TABLE 2: Relative Energies^a (kcal/mol) of $(BN)_2$ Isomers

	II ($^3B_{2g}$)	**I** ($^3\Pi$)	**I** ($^3\Sigma$)	**II** (^1A_g)	**I** ($^1\Sigma$)
HF/6-31 g*	18.99 (1)	0.00 (0)	4.04 (0)	59.30 (0)	62.89 (0)
MP2/6-31 g*	0.00 (0)	4.19 (0)	23.73 (0)	22.23 (0)	68.30 (0)
MP2(full)/ 6-311+g(2d)	0.00 (0)	0.69 (0)	19.69 (0)	15.66 (0)	63.49 (1)
CCSD(T)/6-31 g*	0.00	3.10	14.43	25.31	46.62

[a] Number of imaginary normal vibrational modes in parentheses.

and theoretical attention.[61,62] In large part, this is because of the competitive energy of the linear ($^3\Sigma_g^-$) and rhombic (^1A_g) isomers as the global minimum. The most extended calculations[61,63] indicate the rhombic form is preferred by about 1.0 kcal/mol. However, the energy difference is sensitive to the basis sets and correlation methods. The relative energies (E_{rel}), with the number of imaginary frequencies, of these two isomers obtained in the present calculation are summarized in Table 1. At the HF level, the linear $^3\Sigma_g^-$ form is preferred by about 24 kcal/mol. It is well-known that the Hartree−Fock level does not provide satisfactory energy differences between singlet and triplet isomers. An improved trend of stability is found at the MP2 level where ^1A_g rhombic is most stable. The energy difference between rhombic and linear is reduced to 4 kcal/mol with extension of the basis set. At the CCSD(T)/6-31G* level of theory, this difference is only 2.5 kcal/mol, about twice that of the most accurate theoretical value reported previously.[61,63] Our goal in the present study is not to establish benchmark numbers, rather we are more interested in obtaining trends with reasonable accuracy, trends that are preserved when the basis sets and correlation methods are improved. The other plausible electronic states ($^1\Delta_g$, $^3\Sigma_u^+$, and $^3B_{3u}$) of C_4 are higher in energy by 11−28 kcal/mol and, therefore, are clearly not favored energetically.

Compared to the enormous amount of studies on C_4, investigation of the BN dimer is at a preliminary level.[59,60] The existence of the $(BN)_2$ molecule in the linear form has recently been confirmed experimentally.[59] We have considered both linear and rhombic isomers in both singlet and triplet states, and the relative energies are displayed in Table 2. For all geometries, two of the triplet spin states are found at a much lower energy than are the singlets. This result contrasts with C_4, where the rhombic singlet is preferred. At the HF/6-31G* level, the lowest state is the linear $^3\Pi$, followed by linear $^3\Sigma$. The rhombic $^3B_{2g}$,which is 19 kcal/mol higher in energy, has an imaginary frequency, indicating it is not a true minimum at this level. Electron correlation alters the findings: rhombic $^3B_{2g}$, now a true minimum, is found to be the most stable configuration. However, the linear ($^3\Pi$) and rhombic ($^3B_{2g}$) isomers of $(BN)_2$ are almost isoenergetic, and the E_{rel} value is highly sensitive to basis sets and correlation methods. The same is true of C_4, albeit different electronic states are involved. Extension of basis set from double-ζ (6-31G*) to triple-ζ (6-311+G(2d)) at the MP2 level reduces the E_{rel} value from 4.2 to only 0.7 kcal/mol. (It is worthwhile to mention that this change is not only due to basis-set extension, but also in part due to incorporating inner-shell electrons into the correlation methods.) An energy difference of about 3 kcal/mol is found at the CCSD(T)/6-31G* level. The energy ordering is in accordance with the QCISD(T)/6-31G*//HF/6-31G* results.[59] The next two lowest states, linear $^3\Sigma$ (which resembles the $^3\Sigma_g^-$ state of C_4) and rhombic ^1A_g are also approximately isoenergetic at the MP2 levels. A thorough investigation using more extended basis sets and different correlation methods seems inevitable for the BN dimer.

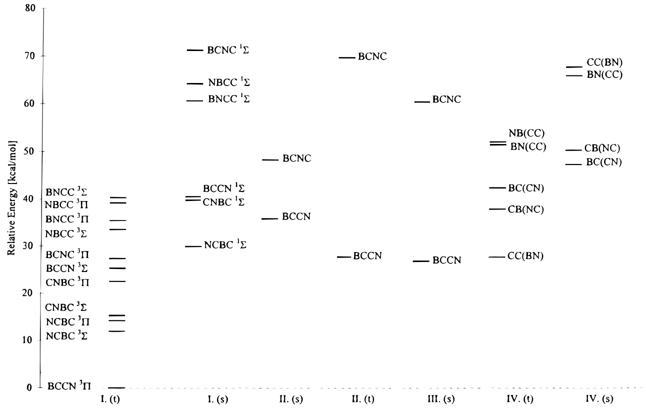


Figure 1. MP2/6-31G* energy diagram for BC_2N, where s and t stand for singlet and triplet, respectively.

Since most of the previous theoretical investigations used ideas about cohesive energies to establish structural stability, the findings of such calculations on BC_2N should be discussed. According to this method, cyclic isomers, because of an extra bond, will be of higher energy (more stable) than the corresponding linear forms. Moreover, the BNCC arrangement in both linear and cyclic forms is the most favorable, followed by the linear forms of NBCC, CNBC, BCCN, BCNC, and NCBC. The E_{rel} values, calculated at different levels of theory, of all possible structural forms (both singlet and triplet) of BC_2N are summarized in Table 3, and their MP2/6-31G* energy order is depicted in Figure 1. With a few exceptions, most of the isomers have a zero imaginary frequency, indicating a true minimum. In some cases, optimization of bent or cyclic structures converged to the linear form. In general, the triplets of BC_2N (like BN dimer) are energetically more favorable than singlets, whereas the reverse order is found in triatomic BCN by Martin and Taylor.[52] They also noted that extension of the basis set from triple-ζ to quadruple-ζ has little effect on the relative energies of BCN. This is also true in the present case where DZ and TZ basis sets are used. While investigating BN-substituted benzene and naphthalene, Kar et al.[64] found that diffuse functions are not so important for the structure and stability of BN-substituted hydrocarbons.

In contrast to both C_4 and $(BN)_2$, the linear BCCN $^3\Pi$ state is the most stable isomer at all levels of theory. Indeed, the cyclic (**II**) structures are quite a bit higher in energy. This atomic ordering is inconsistent with the cohesive energy calculations where isomers with BN and CC fragments are preferred over those with direct CN and BC bonds. However, evidence of significant BC and CN bonds in BC_2N materials has been reported experimentally.[22,25,39] Kawaguchi et al.[38] suggested that B−C−C−N and B−N together are the basic building block from which the structure of BCN graphite-like materials can be generated by repetition. It is interesting to note that in the triatomic BCN molecule, BNC ($^1\Sigma^+$) is the global minimum followed by the BCN $^1\Sigma^+$ state by 10 kcal/mol.[52] Thus, substitution of C_2 by the BN unit in C_3 and C_4 clusters results in different structural features. In the triatomic, the singlets are more stable, whereas triplets are favored in the

TABLE 3: Relative Energies[a,b] (kcal/mol) of BC_2N Isomers

		I ($^3\Pi$)	**I** ($^3\Sigma$)	**I** ($^1\Sigma$)	**II** ($^1A'$)	**II** ($^3A''$)	**III** ($^1A'$)	**IV** ($^1A'$)	**IV** ($^3A''$)
BCCN	A	0.00 (0)	5.09 (0)	55.77 (1)	69.27 (0)	39.15 (0)	55.23 (0)	53.62 (0)	44.25 (0)
BC(CN)[c]	B	0.00 (0)	25.34 (0)	N/A	35.88 (0)	27.80 (0)	26.91 (0)	47.40 (0)	42.51 (0)
	C	0.00 (0)	N/A	50.54 (2)	39.06 (0)	31.34 (0)	26.65 (0)		
	D	0.00	N/A	N/A	35.50	28.51	15.69[d]		
BCNC	A	22.89 (0)	166.00 (2)	71.30 (1)	73.13 (0)	76.66 (0)	69.51 (0)	N/A[e]	43.74 (0)
CC(BN)[c]	B	27.40 (0)	196.27 (1)	71.29 (2)	48.34 (0)	69.80 (1)	60.48 (0)	67.88 (0)	27.79 (0)
	C	27.01 (0)	N/A	69.46 (2)	51.98 (0)	N/A	60.33 (0)		
	D	26.30	N/A	N/A	46.09	N/A	N/A		
CBNC	A	6.05 (1)	0.85 (0)	35.88 (0)				N/A[e]	22.39 (0)
CB(NC)[c]	B	22.50 (0)	15.20 (0)	39.82 (0)				50.44 (0)	37.98 (0)
	C	22.23 (0)	14.23 (0)	38.58 (0)					
	D	19.00	11.09	29.46					
NCBC	A	4.00 (0)	3.17 (0)	38. 77 (0)				N/A[e]	N/A[e]
NC(BC)[c]	B	14.12 (0)	11.90 (0)	29.97 (0)					
	C	13.73 (0)	10.94 (0)	29.53 (0)					
	D	10.28	6.28	23.82					
								IV. $^1A_1$	**IV**.$^3B_1$
BNCC	A	28.78 (1)	30.17 (0)	62.75 (1)				66.15 (0)	77.97 (0)
BN(CC)[c]	B	35.42 (0)	40.32 (0)	60.6 4 (0)				66.04 (0)	51.56 (0)
	C	34.04 (0)	36.80 (0)	58.71 (1)					
	D	33.59	38.60	48.18					
NBCC	A	22.11 (0)	13.92 (0)	70.38 (0)				80.32 (1)	54.55 (0)
NB(CC)[c]	B	39.19 (0)	33.49 (0)	64.26 (0)				112.39 (1)	52.18 (0)
	C	39.80 (0)	33.59 (2)	63.63 (0)					
	D	32.84	25.51	N/A					

[a] Number of imaginary normal vibrational modes in parentheses. [b] A, B, C, and D of second column refer to HF/6−31 g*, MP2/6−31 g*, MP2(full)/6-311+g(2d), and CCSD(T)/6−31 g*, respectively. [c] See Scheme 1 for atomic arrangement of structure **IV**. [d] MP2(full)/6-311+g(2d) optimized geometry. [e] Converges to a linear, bent, or rhombic form.

tetraatomic. Another remarkable difference is the atomic arrangement. The isomer with a BN bond in the triatomic system is the most stable one, in contrast to the tetraatomic system where B and N atoms prefer the terminal positions. It seems the structure of BN-substituted carbon materials highly depends on the cluster size. However, it is very important to consider larger BN-substituted carbon clusters, namely, BC_3N, B_2CN_2, BC_4N, $B_2C_2N_2$, etc., before proposing a general conclusion.

The next lowest energy states of BC_2N within 20 kcal/mol are also in the linear form, and the E_{rel} order is NCBC ($^3\Sigma$) < NCBC ($^3\Pi$) ≈ CNBC ($^3\Sigma$) < CNBC ($^3\Pi$). Surprisingly, none of these contain both BN and CC bonds. Isomers with these bonds are proposed to be more stable according to previous predictions. Triplet BNCC and NBCC where both bonds exist are 30−40 kcal/mol (50−60 kcal/mol in case of singlets) higher than the global minimum. Isomers with a terminal B atom prefer the $^3\Pi$ over the $^3\Sigma$ state, but the latter state is more stable when one of the carbon atoms is at the end of the chain. Imaginary frequencies in singlet BCCN and BCNC led us to consider possible bent isomers (**III** in Scheme 1). In fact, the $^1A'$ state of bent BCCN (**III**) is found to be higher than the linear BCCN $^3\Pi$ state by 27 kcal/mol according to the MP2 method. A closer look at Table 3 and Figure 1 reveals that isomers (linear and bent) with a terminating nitrogen atom are, in general, more stable. This may be due to the position of the lone pair of N which may lie outside the chain. Since nanotubes or coils can be constructed by bending the BC_2N sheets, it is interesting to monitor the variation of the energy upon bending the molecule. It can be seen from Figure 2 that less than 3 kcal/mol is required to bend the BCC bond of BCCN $^3\Pi$ (slightly more flexible than CCC bonds in C_4) by about 30°. On the other hand, the CCN bond is harder to bend.

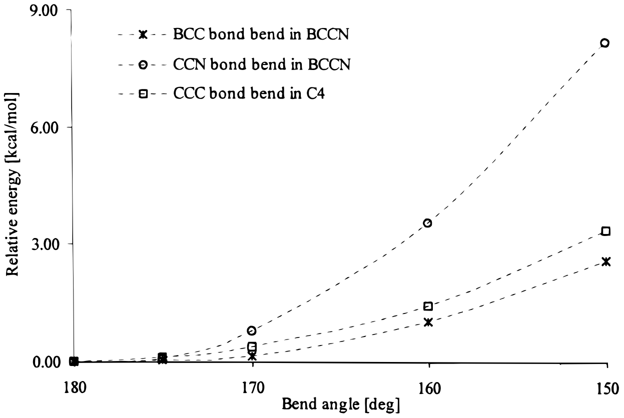


Figure 2. Energy required to bend $^3\Sigma_g^-$ C_4 and $^3\Pi$ BCCN. Energies relative to the corresponding MP2(full)/6-311+G(2d) minimum.

Surprisingly cyclic (**II**) isomers (most stable in C_4 and B_2N_2) of BC_2N are less stable than the bent ones. The lowest cyclic BCCN $^3A''$ is about 28 kcal/mol (CCSD(T)/6-31G*) above the most stable isomer with the same atomic order. The singlet−triplet energy difference in this cyclic (**II**) form, where both BN and CC bonds exist, is 7 kcal/mol. Even less stable than cyclic BCCN are BCNC isomers (no BN and CC bonds). This result leads to the conclusion that cyclic structures may prefer BN as well as CC bonds, in contrast to the linear form. In the case of BN−benzene and BN−naphthalene, B and N atoms are always together and BN bonds tend to aggregate with one another.[64] The E_{rel} values of the fourth possible atomic arrangement **IV** in Scheme 1 are given in the last two columns of Table 3. Again triplets are more stable than the singlets. Only one triplet, CC(BN), is within 30 kcal/mol of the global minimum at the MP2 level.

It will be important to investigate possible isomerization processes, i.e., how easily one isomer can convert to other forms. In the case of triatomic BCN, a barrier of about 30 kcal/mol[52] indicates that interconversion of BNC to BCN would not be favored. Looking at the atomic arrangement in different isomeric forms of the tetraatomic, it was found that in most of the cases isomerization might occur via a cyclic (similar to **IV** in Scheme 1) transition state (TS). Although some reactants

TABLE 4: Geometries[a] of Most Stable Linear Isomers of BC_2N

	r_{AB}	r_{BC}	r_{CD}		r_{AB}	r_{BC}	r_{CD}
BCCN $^3\Pi$	1.349	1.357	1.156	CNBC $^3\Sigma$	1.170	1.381	1.433
	1.364	1.376	1.163		1.199	1.392	1.459
	1.360	1.372	1.152		1.188	1.388	1.453
	1.374	1.362	1.190		1.202	1.391	1.466
NCBC $^3\Sigma$	1.151	1.494	1.426	CNBC $^3\Pi$	1.169	1.382	1.368
	1.135	1.522	1.459		1.190	1.406	1.337
	1.127	1.519	1.453		1.180	1.401	1.331
	1.177	1.497	1.461		1.198	1.397	1.370
NCBC $^3\Pi$	1.145	1.488	1.380				
	1.147	1.511	1.323				
	1.143	1.506	1.315				
	1.173	1.496	1.371				

[a] Four values refer to HF/6−31 g*, MP2/6−31 g*, MP2(full)/6-311+g(2d) and CCSD(T)/6−31 g* levels, respectively. Bond lengths in Å.

TABLE 5: Geometries[a] of Most Stable Cyclic and Bent Isomers of BC_2N

	r_{AB}	r_{BC}	r_{CD}	r_{DA}	a_{ABC}	a_{BCD}	a_{CDA}
BCCN **II** ($^3A''$)	1.696	1.310	1.308	1.473	58.78	135.90	65.63
	1.609	1.345	1.335	1.496	60.48	131.73	63.94
	1.605	1.337	1.325	1.491	60.80	131.59	64.38
	1.567	1.356	1.362	1.498	62.53	127.70	64.37
BCCN **II** ($^1A'$)	1.509	1.580	1.325	1.372	63.45	110.40	74.13
	1.592	1.479	1.337	1.475	66.26	117.25	73.23
	1.593	1.479	1.330	1.474	66.48	117.03	73.75
	1.583	1.509	1.340	1.453	65.74	115.40	73.79
BCCN **III** ($^1A'$)	1.562	1.343	1.161		143.08	179.65	
	1.371	1.428	1.187		107.30	173.01	
	1.362	1.419	1.176		111.25	172.99	

[a] Four values refer to HF/6-31g*, MP2/6-31g*, MP2(full)/6-311+g(2d), and CCSD(T)/6-31g* levels, respectively. Bond lengths in Å and angles in deg.

and products are isoenergetic or within 10 kcal/mol, the cyclic (**IV**) isomers are, in general, well above 25 kcal/mol, indicating a high barrier. For example, linear CNBC (triplet) to linear triplet NCBC isomerization might pass via the CB(CN) TS state where the barrier height is above 20 kcal/mol (MP2/6-31G*). Another possibility of atomic rearrangement is via a cyclic/rhombic (**II**) form where the process seems more difficult in the sense that two terminal bonds of linear isomers have to be bent to form cyclic isomers. Thus, the isomerization reactions may be favorable thermodynamically but certainly not kinetically because of the high barrier. Once the isomer is formed with a particular atomic arrangement, it will retain that form and can only be converted to other isomeric forms under extreme conditions such as high temperature and pressure.

B. Structure and Nature of Bonding. Fully optimized geometries of first few most stable isomers of BC_2N are reported in Tables 4 and 5. For the sake of comparison, the geometries of C_4 and BN-dimer are given in Table 6. Since different correlation methods, in general, computed bond lengths and angles fairly close to one another, we will mostly concentrate on MP2(full)/6-311+G(2d) values. Compared to standard bond lengths, we found the BC (1.360 Å) bond in the lowest $^3\Pi$ BC_2N is considerably shorter than the single bond (1.54 Å), CC (1.372 Å) is longer than a double bond (1.339 Å in ethylene), and CN (1.152 Å) is close to a triple bond (1.153 Å in HCN). A similar picture emerges from bond index analyses(Table 7) and from a localization picture (not shown here). The BC bond contains three α and two β electrons (double bond and one unpaired electron, the other unpaired electron is located on the boron atom) with a bond index of 2.1, somewhat between double and triple bonds. CC is a single σ bond with bond index 1.03 and CN contains one σ and two π bonds. The bond index of the CN bond is 2.55, indicating a partially polarized triple bond. (Polarization of a bond tends to lower the bond index.) This is also the case in the BC bond, where the bond is polarized toward C because of higher electronegativity of carbon.

Compared to BN, NC, and CC bonds, the BC bond in linear isomers is found to be most sensitive to its position in the chain and also on the electronic state. The inner bond is about ∼1.51 Å long and insensitive to the states ($^3\Pi$ and $^3\Sigma$). Clearly, this is a single bond with $I_{BC} \approx 1.0$. On the other hand, the terminal BC bonds are shorter and vary from state to state; the $^3\Pi$ state of NCBC and CNBC contains the shortest BC bond (∼1.32

TABLE 6: Geometries[a] of Most Stable Isomers of C_4 and $(BN)_2$

	r_{AB}	r_{BC}	a_{ABC}	a_{BCD}		r_{AB}	r_{BC}	a_{ABC}	a_{BCD}
C_4 **II** (^1A_g)	1.425	1.425	61.51	118.49	BNBN **II** ($^3B_{2g}$)	1.418	1.418	68.81	111.19
	1.454	1.454	63.29	116.71		1.433	1.433	68.03	111.94
	1.451	1.451	63.84	116.16		1.427	1.427	68.20	111.80
	1.455	1.455	62.59	117.41		1.444	1.444	67.69	112.31
C_4 **I** ($^3\Sigma_g^-$)	1.299	1.276			BNBN **I** ($^3\Pi$)	1.245	1.362		
	1.315	1.298				1.266	1.373		
	1.307	1.291				1.260	1.367		
	1.323	1.301				1.269	1.375		

[a] Four values refer to HF/6-31g*, MP2/6-31g*, MP2(full)/6-311+g(2d), and CCSD(T)/6-31g* levels, respectively. Bond lengths in Å and angles in deg.

TABLE 7: Two- (I_{AB}) and Three-Center (I_{ABC}) Bond Indices of Most Stable Isomers of C_4, $(BN)_2$, and BC_2N

	I_{AB}	I_{BC}	I_{CD}	I_{DA}	I_{AC}	I_{BD}	I_{ABC}	I_{BCD}	I_{CDA}	I_{DAC}
C_4 **I** ($^3\Sigma_g^-$)	2.05	1.76	2.05				−0.04	0.00		
C_4 **II** (^1A_g)	1.11	1.11	1.11	1.11	1.02	0.16	0.22	0.04	0.22	0.04
BNBN **II** ($^3B_{2g}$)	1.18	1.18	1.18	1.18	0.63	0.11	0.18	−0.00	0.18	−0.00
BNBN **I** ($^3\Pi$)	2.11	1.16	2.03				0.07	−0.02		
BCCN **I** ($^3\Pi$)	2.11	1.03	2.55				−0.07	−0.05		
NCBC **I** ($^3\Sigma$)	2.67	0.98	2.08				0.00	0.01		
NCBC **I** ($^3\Pi$)	2.73	1.04	1.94				−0.02	0.05		
CNBC **I** ($^3\Sigma$)	2.17	1.02	2.02				0.02	−0.01		
CNBC **I** ($^3\Pi$)	2.21	1.02	1.98				0.00	0.02		
BCCN **II** ($^3A''$)	0.89	1.57	1.28	0.93	0.73	0.14	0.28	0.14	−0.06	−0.01
BCCN **II** ($^1A'$)	0.99	0.98	1.50	1.15	0.72	0.14	0.05	0.05	0.18	0.00
BCCN **III** ($^1A'$)	2.20	1.17	2.58	0.19	0.10	0.02	0.07	−0.04	−0.02	0.02

Å), while this length increases to 1.45 Å in their $^3\Sigma$ states. The bond indices are close to 2 in both cases despite a substantial difference in bond lengths. The origin of this difference can be understood from LMOs. In $^3\Pi$ states, there are five electrons (3α and 2β) between B and C and the terminal carbon contains an unpaired α electron, whereas in $^3\Sigma$, one of the β electrons from the BC bond of $^3\Pi$ is shifted to C to form a lone pair. This change makes BC bonds weaker and longer in $^3\Sigma$ states. The presence of the lone pair on the terminal carbon is associated with the extra stability of $^3\Sigma$ states over $^3\Pi$ states. The CN distances in all the isomers are in the 1.188−1.127 Å range, indicating a triple bond. The multiplicity of the CN bond in triatomic BCN is also close to 3 in both BNC and BCN arrangements.

In general, the outer bonds in the most stable isomers of linear BC_2N are triple or between double and triple and the inner one is always slightly shorter than a single bond, irrespective of the combination of atoms. This bonding pattern is almost the same as that found in linear $^3\Pi$ $(BN)_2$ (see Tables 6 and 7) but differs considerably from the most stable linear C_4 where all three bonds are double in nature. It is well-known that the isomer of C_4 with alternating triple and single bonds is less stable.[65] The three-center bond indices in all cases are not significant, indicating a localized pattern of bonding.

Let us turn our attention to cyclic (**II**) isomers of BC_2N (Table 5) and compare the results with C_4 and BN dimer (Table 6). The CC bond in the most stable cyclic isomer ($^3A''$) of BC_2N is shorter than the corresponding distance in C_4, whereas the BN bond is slightly longer compared to the BN distance in BN dimer. Unlike linear isomers, the length of the CN bonds is significantly (0.15−0.33 Å) longer than a typical CN triple bond. The fourth type of bond in the cyclic isomers is the BC bond which is the longest one (1.60 Å) and clearly a pure single bond. However, a slightly shorter (1.47 Å) BC bond is also found in the singlet cyclic BC_2N. The bond indices, given in the lower part of Table 7, are in agreement with these results. It may be noted that due to the electronegativity difference of B, C, and N, the bonds are mostly ionic and, hence, the 2c-bond indices deviate from integral values, 1 for single, 2 for double, etc.

Alternating sharp and blunt bond angles are found in cyclic/rhombic (**II**) C_4, $(BN)_2$ and BC_2N (both singlet and triplet states). The BCC angle of cyclic BC_2N is the sharpest and close to $C_1C_2C_3$ of C_4 and BNB of $(BN)_2$. The widest CCN angles in the hybrid system are, however, 15−20° more open than $<C_2C_3C_4$ and $<$NBN of the parent systems. The other sharp and blunt angles are CNB and NBC, respectively. In the case of $(BN)_2$, the angles are sharp when nitrogen is in the center, otherwise they are blunt. No such correlation exists in the BC_2N case.

An interesting feature of bonding in C_4, $(BN)_2$, and BC_2N has been found from bond index calculations. All three molecules in their cyclic (**II**) form contain three-center (3c) bonds which have not been reported earlier. It can be seen from Table 7 that some of the 3c-bond index (I_{ABC}) values are positive and significant. It is by now well-established[56] that for a 3c-bond, this value is greater than 0.1. The parent molecules contain two 3c-bonds which are symmetric and reside on the sharp angle regions. $I_{C_2C_3C_4}$ and I_{NBN} of C_4 and BN dimer, respectively, are close to zero, i.e., no 3c-bond in the blunt zone. Interestingly, BC_2N also contains two three-center bonds. However, their position is not the same as in parent molecules. I_{BCC} (sharp) and I_{CCN} (blunt) are significant, and the former bond is stronger than the latter. The other factor involved in 3c-bonding is the significant interaction between the nonbonded atoms. For example, $I_{C_1C_3}$ in C_4, I_{BB} in $(BN)_2$, and I_{BC} in BC_2N values are in the range of 0.6−1.0. These large values of I_{AC} in Table 7 should, therefore, not be anticipated as a standard single bond.

TABLE 8: Atomization Energies (ΣD_e)[a] (kcal/mol), Electron Affinities (EA), and First Ionization Potentials (IP) (eV) of the Most Stable C_4, $(BN)_2$, and BC_2N Isomers

	MP2/ 6-311+g(2d) ΣD_e	CCSD(T)/ 6-31g* ΣD_e	MP2/6-311+g(2d)	
			EA	IP
C_4 **II** (^1A_g)	474.8	408.4	2.454	10.695
C_4 **I** ($^3\Sigma_g$-)	470.8	405.9	3.563	11.023
	437.9[b]			
$(BN)_2$ **II** ($^3B_{2g}$)	403.1	332.1	2.773	10.144
$(BN)_2$ **I** ($^3\Pi$)	402.4	329.0	2.816	9.717
BCCN **I** ($^3\Pi$)	453.0	381.7	3.344	10.316
NCBC **I** ($^3\Sigma^-$)	442.1	375.4	2.671	10.060
NCBC **I** ($^3\Pi$)	439.3	371.4	3.137	10.312
CNBC **I** ($^3\Sigma^-$)	438.8	370.6	2.198	9.619
CNBC **I** ($^3\Pi$)	430.8	362.7	2.799	14.900

[a] Uncorrected for ZPVE, no other correction term. [b] G1 value from ref 63.

Finally, the optimized geometric parameters of trans-bent (**III**) isomer of BC_2N, given in Table 5, show similar bond lengths as in the linear $^3\Pi$ isomer except a slight elongation of the inner CC bond. As discussed in the previous section, the BCC bond is found to be more flexible than the CCN bond. The CCN bond is almost linear, and the BCC angle is within the 107−110° range at the MP2 level. The BCN angle of the less-stable bent BCNC isomer (not shown in Table 6) is around 124°, and like CCN in the BCCN isomer, the CNC bond is almost linear. These results provide qualitative ideas about bending the BCN sheet into nanotubes: the region of BCC or BCN is likely to be the preferred site of bending rather than CCN or CNC.

C. Thermochemistry. It is important to assess the stability of the BC_2N isomers and compare with isoelectronic C_4 and $(BN)_2$. One way to compare the stability of the clusters with different atomic composition is to look at their total atomization energies (ΣD_e). These energies of the lowest isomers are presented in Table 8. The accuracy of ΣD_e values depends on the theoretical methods used. MP2 generally overestimates the true value, while CCSD(T) underestimates the same. The G1 method usually predicts[66] more accurate atomization energies, within 2 kcal/mol of the experimental values. It can be seen from Table 8 that the MP2 atomization energy of C_4 is 33−37 kcal/mol higher than the G1 value, and the corresponding CCSD(T) value is underestimated by the same amount. Thus, it seems that the atomization energies of the other species will be somewhere between the MP2 and CCSD(T) values, possibly in the midle of the range. Although the G1 value of C_4 is not accurate enough, as pointed out by Martin et al.,[63] the present calculated values will provide a qualitative sense of the stability of the parent and hybrid system. From the results it is clear that the stability of the lowest BC_2N will be between C_4 and $(BN)_2$.

The vertical electron affinities (EA) and ionization energies (IE) calculated using the MP2/6-311+G(2d) level are also listed in Table 8. Again, these values cannot be considered as quantitative because the geometries of the ions were not relaxed and the level of the theory used is not extensive. The EA values suggest that for all systems the negative ions will be stable. Compared to carbon and isoelectronic $(BN)_2$, the most stable isomer of the mixed system has a higher EA value and the IP value is between the pure systems.

Conclusion

To our knowledge, this is the first thorough and high-level ab initio investigation on the BC_2N molecule, the basic unit of BCN materials. The structure, stability, and nature of the bonding of BC_2N have been compared with the tetraatomic carbon and BN molecules, and the main findings of the present investigation are as follows. The most stable structure of BC_2N is linear, whereas C_4 and $(BN)_2$ are cyclic. In C_4 and $(BN)_2$, the linear and cyclic structures are isoenergetic, BN or CC substitution leads to a preference for the linear form by more than 25 kcal/mol. Contrary to C_4, the triplet states of both BC_2N and $(BN)_2$ are preferred over singlets. The atomic arrangement in linear isomers depends on the size and also on the number of carbon atoms in the cluster. No definite trend has been identified as yet. In contrast to linear forms, the cyclic isomers prefer B and N together, i.e., BNCC arrangement. Because of the high barrier, interconversions from one atomic arrangement to another are possible only at a very high temperature or pressure. The bonding in most stable linear isomers of BC_2N and $(BN)_2$ is polyacetylenic type (outer bonds are triple bonds and the inner one is a single bond), in sharp contrast to cumulenic bonding in C_4. Three-center bonds are found in all cyclic isomers. Total atomization energies indicate that the stability of the mixed system lies between C_4 and $(BN)_2$.

The present study presents several additional questions about this interesting and important class of systems. For example, one might wonder about the structure of dimer, trimer, etc., of BC_2N and the effect of the number of C, B, and N atoms on the structure and properties of $B_xC_yN_x$. Some of these studies are under investigation by the present authors.

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