NEW CHAINS OF BORON-CARBON AND BORON-CARBON HYDRIDS

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Ab initio quantum chemical methods were applied to investigate the ground state energies and geometrical configurations of boron-carbon $(BC)_n$ and boron-carbon hydrides $(HBCH)_n$ chains. The boron-carbon chains were found to be unstable in one dimension. They dissociate into boron-carbon dimers or transform into two dimensional network. The boron-carbon hydride chains were found to be stable in one dimensional structure with bond alternation. The *ab initio* ground state energies of the conjugated $(HBCH)_n$ chains were fitted into the SSH model, in order to determine the corresponding parameters for the ground state energy. According to the SSH model, this conjugation induces a band gap of around 0.8 eV.

Key words: polymer, band gap, tight binding model, boron-carbon, boron-carbon hydrids, chain.

1. INTRODUCTION

The combination of boron and other chemical elements leads to the formation of variety of materials possessing interesting physical and structural properties. The existence of an unpaired electron in boron, having three-bonding functions, provides the possibility of forming different stable one, two and three dimensional configurations of pure boron, as linear chains [1], quasi-planar [2], tubular [3, 4] and spherical [5].

Boron occurs in nature in several well known crystal forms, two of which contain units of strongly bound B_{12} icosahedra [6]: The α- and β-rhombohedral boron. The presence of weak three-center bonds in α-rhombohedral boron is responsible for its weak thermal stability. This configuration transforms into the β one at high-temperature around 1200°C. Beside that, boron forms strong chemical bonds with other elements due to its unoccupied p valence orbitals and its short covalent radius. Such compounds are, borides, boranes, boron hydrids

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and metallic-boron. These boron compounds have many important industrial applications in high-temperature semiconductors, high density fuels [7] and aerospace industry [8, 9]. Therefore, boron compounds in general and boron carbide in particular were the subject of interest of many authors recently.

The crystal structure and electronic structure of boron halides B_9X_9 (X = Cl, Br, I) and B_4H_4 has been reported by Hönle *et al.* [10] using X-ray methods and quantum chemical calculations. The ground and excited states of an icosahedral $B_{12}H_{12}$ cluster simulating B_{12} cluster in β rhombohedral boron have been calculated by Fujimori and Kimura [11] using the *ab initio* SCF-MO method. B-C-N nanotubes and boron doping carbon nanotubes are synthesized by Redlich *et al.* [12]. Recently, small boron-carbon chains have been stabilized in rare earth metallic framework by Bauer *et al.* [13] using extended Hückel tight-binding and *ab initio* calculations.

For more understanding of the physical and chemical properties of boron compounds in general and boron-carbon composites in special, we devote this work to study the boron-carbon chains using *ab initio* quantum chemical methods and the (SSH) model which is based on the tight binding approximation.

2. THEORETICAL MODELS

A. For the purpose of total energies calculations, electronic structures and equilibrium geometries we have used the Hartree-Fock self-consistent-field approximation (HF-SCF) and the Møller-Plesset perturbation theory of second order (MP2). The above *Ab initio* quantum chemical methods have been applied into both $(BC)_n$ and $(HBCH)_n$ chains using different STO3G, 3-21G and Double-ζ (DZ) basis sets for singlet ground states. Only doublet ground states could not be calculated at the MP2 level, because the used MP2-code is not available for open-shell systems. Three degrees of freedom for a boron-carbon chain r_1, r_2 and θ (Fig. 1a) have been chosen to allow bond alternation between successive boron atoms. While $(HBCH)_n$ chain has two extra which are the B-H and C-H bonds. The starting values of these parameters were chosen arbitrary to find the local minima on the energy hypersurface. The ground state energies of different sizes of boron chains were calculated firstly using the STO3G basis set. Hereafter the obtained structure is used as an input for a re-optimization using the 3-21G basis set at the HF-SCF level of theory.

Further optimisations at the MP2 Level were done for selected structures of closed-shell systems only. The final values of optimized parameters are recorded at the lowest total energies for both chains.

B. The SSH Model is introduced 1979 by Su, Schrieffer and Hegeer [14] to describe the physical properties of a single chain of polyacetylene $(CH)_n$. We can

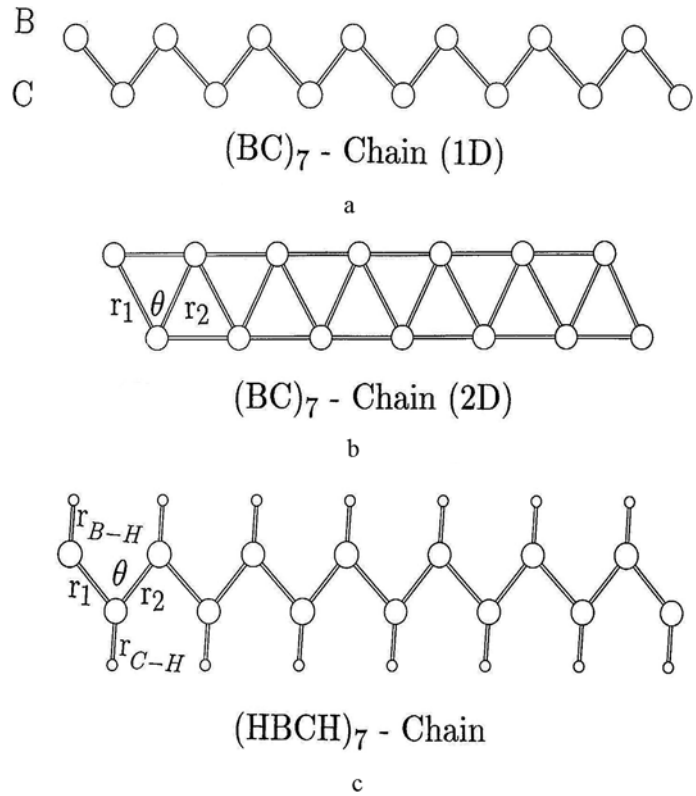

Fig. 1 – a) The one dimensional $(BC)_7$ chain, arising from BC-bonds between two linear boron and carbon chains, is energetically unstable. It transforms into b) the two dimensional $(BC)_7$ chain where the inter-atomic distances r_1 and r_2 correspond to single and double bonds in boron-carbon and in c) boron-carbon hydrogen $(HBCH)_7$ chains.

assume that σ electrons are rigid and the π electrons move along the chain. Therefore, the model Hamiltonian is the sum of the electronic and the potential terms respectively. *i.e.*

$$H = -\sum_{is} t_{i+1,i}(C^{\dagger}_{i+1,s}C_{i,s} + C^{\dagger}_{i,s}C_{i+1,s}) + \frac{K}{2}\sum_{i}(u_{i+1} - u_i)^2. \tag{1}$$

Where K is the effective σ spring constant and u_i is the displacement of the i-th (CH) group. And, $t_{i+1,i} = t_0 - \alpha(u_{i+1} - u_i)$ where t_0 is the hopping integral for the unconjugated chain and α is the electron-lattice displacement (phonon) coupling constant. $C^{\dagger}_{is}$ (C_{is}) are the creation (annihilation) operators which create (destroy) π electrons of spins $s\left(\mp\frac{1}{2}\right)$ on the i-th (CH) group. The

diagonalization of Eq. 1 gives the ground state energy in terms of u [14]. *i.e.*

$$E(z) = -\frac{4nt_0}{\pi}\left[1 + \frac{1}{2}\left(ln(4/z) - \frac{1}{2}\right)z^2 + \ldots\right] + \frac{nKt_0^2 z_0^2}{2\alpha^2} \tag{2}$$

where $z(u) = \frac{2\alpha u}{t_0}$ and $z_0 = z(u_0)$. This model is usually used to study organic polymers rather than the inorganic ones. Nevertheless, recently it was applied to inorganic $(BN)_n$ [15], and boron hydride $(BH)_n$ chains [1].

3. RESULTS AND DISCUSSION

3.1. BORON-CARBON CHAINS

A *Z*-matrix for different sizes of boron-carbon chains is designed to allow only bond alternation between two successive bonds r_1, r_2 and the angle between the two bonds θ. The resulting one dimensional configuration is unstable. It transforms into two dimensional $(BC)_n$ chain as shown in Fig. 1b. Adding the hydrogen atom to B and C atoms insures the stability of the chain as we will see later. The final energies are recorded in Table I with the binding energies. The binding energy per (BC) unit $E_b(BC)/n$ is defined as the difference between the total energy of the chain $E_b((BC)_n)/n$ and the energy of an isolated (BC) unit $E(BC)$, *i.e.*

$$E_b(BC)/n = E(BC) - E((BC)_n)/n. \tag{3}$$

These values which are obtained at 3-21G basis set are plotted in Fig. 2 as a function of n, the (BC) unit number in the chain. This function increases monotonically and converges to an asymptotic limit of the bulk's binding energy per unit for large n.

Table 1

HF-SCF ground state energies of boron-carbon chains for 3-21G basis sets

n	$E(BC)_n$ [a.u.]	$E_b(BC)/_n$ [eV]
1	–61.86133	0.0
2	–124.01915	4.034
3	–126.13412	4.990
4	–248.10074	4.460
5	–310.22296	4.987
6	–372.21383	4.743
7	–434.28948	4.899

Another property which characterizes the boron-carbon chain is the π orbital Mulliken population. This population appears because of the electron transfer from 2S into p_z orbitals. The population of p_z for different sizes of

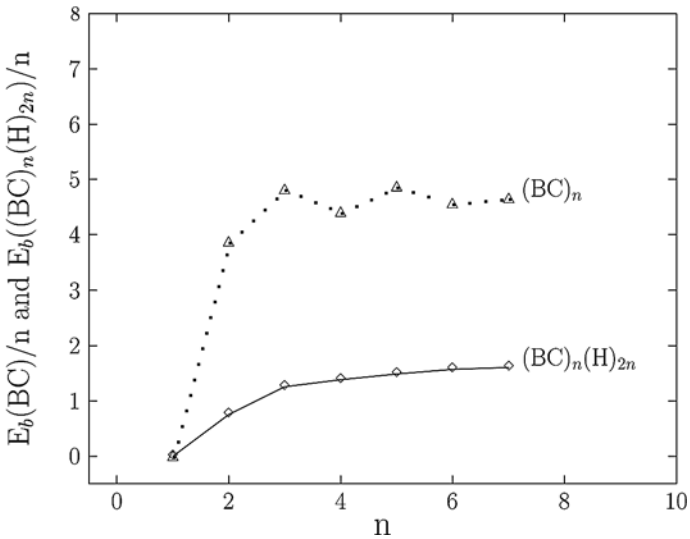

Fig. 2 – The binding energy of boron-carbon chain per (BC) unit (eV) (dotted line, Δ) and the binding energy of boron-carbon hydrids chain per (HBCH) unit (eV) (solid line, ◊).

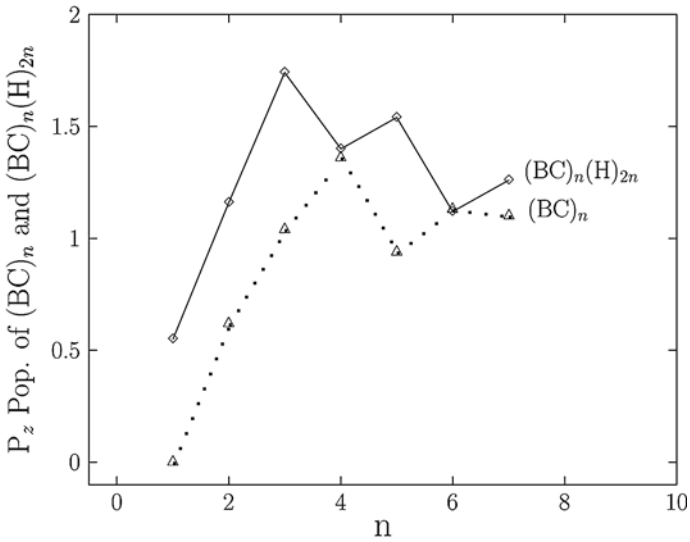

Fig. 3 – The Mulliken population p_z of boron-carbon (dotted line, Δ) and p_z of boron-carbon hydrids (solid line, ◊) chains as a function of chain size.

boron-carbon chain is shown in Fig. 3. The function of p_z increases with increasing the chain size converging to a limit of 7/8 (7 valence electrons in 8 orbitals) for large n. The overlapping between these partially occupied p_z orbitals stabilizes the two dimensional boron-carbon chains.

3.2. BORON-CARBON HYDRIDE CHAINS

The previous Z-matrix has been modified to suit the Boron-Carbon Hydrids chain. Two further parameters for boron-hydrogen and carbon-hydrogen bonds are added. Five parameters of $(\mathrm{HBCH})_n$ chains are optimized at *ab initio* HF-SCF and MP2 methods using the standard STO3G and 3-21G basis sets. The resultant ground state energies of different sizes of the chains are reported in Table 2. The geometrical structure of the Boron-Carbon Hydride chains is in Fig. 1c showing that it possesses a zigzag structure similar to the boron hydrogen ones, as reported in [1]. Invoking the binding energy per unit concept, Eq. 3 can be rewritten for the binding energy per (HBCH) unit of Boron-Carbon Hydride chains

$$E_b(\mathrm{HBCH})/n = E(\mathrm{HBCH}) - E(\mathrm{HBCH})_n/n, \tag{4}$$

where $E(\mathrm{HBCH})_n$ is the ground state energy of the chain and $E(\mathrm{HBCH})$ is the ground state of the (HBCH) unit. The $E_b(\mathrm{HBCH})/n$ values obtained at the 3-21G basis set are plotted in Fig. 2 as a function of the chain size. The binding energy function increases monotonically up to $n \leq 3$ then it saturates for $n > 4$.

Table 2

HF-SCF ground state energies of boron-carbon hydride chains for 3-21G basis sets

n	$E(\mathrm{HBCH})_n$ [a.u.]	E_b (HBCH)/n [eV]
1	–61.86133	0.0
2	–124.49410	0.815
3	–189.79314	1.287
4	–253.07348	1.395
5	–316.31914	1.280
6	–379.65175	1.690
7	–442.93024	1.600

Another qualitative properties of the stability of the $(\mathrm{HBCH})_n$ chains is the Mulliken population of the π-orbitals. The Mulliken population P_z can be plotted as a function of the chain size n as shown in Fig. 3. This function oscillates at $n > 3$ with increasing n approaching a limit of around 9/8 (9 valence electrons in 8 orbitals). This limit should be increased by larger n due to the conjugation of

the chain. The difference between two successive bonds $\delta r = |r_1 - r_2|/2$ (amount of conjugation in Å) as a function of n (for $n = 6$–14) is plotted in Fig. 4. The curve decreases exponentially approaching 0.028 Å for $n \geq 13$. The case $n = 4$ is not presented in the figure, because the chain energetically prefers two (HBCH) dimers rather than a chain structure.

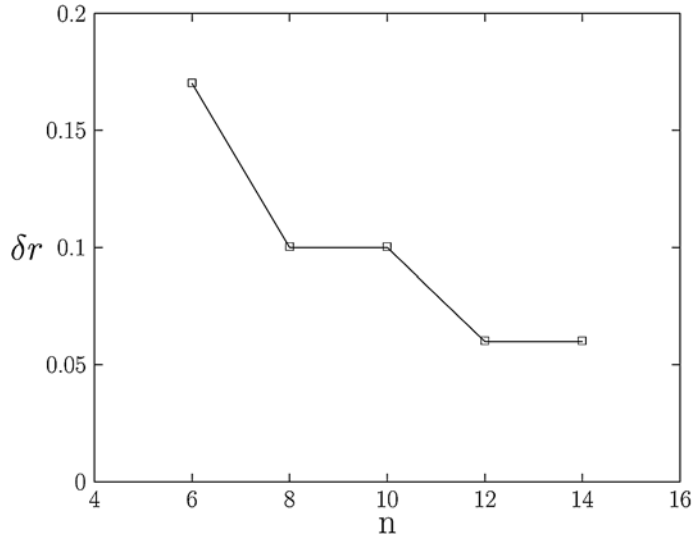

Fig. 4 – The difference δr between two successive bonds in boron-carbon hydrid chain.

In order to make a connection between the *ab initio* results of $(HBCH)_n$ chain and the SSH model we have performed the following steps:

1. We studied the dependence of the ground state energy $E(u)$ on the conjugation coordinate u. In the conjugated chain r_1 and r_2 are displaced by $\pm u$ respectively in their directions. All degrees of freedom of the $(HBCH)_n$ chain (*e.g.*, $n = 12$) were optimized at the MP2 approximation using double zeta (DZ) basis set. The resulting equilibrium bond lengths are $r_1 = 1.508$ Å and $r_2 = 1.567$ Å. They correspond to double and single bonds as in $(BH)_n$ chain. The BH bond in $(HBCH)_n$ is 1.197 Å which is larger than BH bond in $(BH)_n$ chain. The CH bond is 1.096 Å and the angle θ is 115.6°. This gives an equilibrium conjugation of $u_0 = 0.033$ Å. This discrepancy with Fig. 4 is due to electron correlation through MP2. In case of $u = 0$, the optimized degrees of freedom are $r_{B–C} = 1.535$ Å, $r_{B–H} = 1.20$ Å, $r_{C–H} = 1.096$ Å, the angle B – C – B is 114.8°. Using the relation between the bond and the electron hopping which is given by Tanaka *et al.* [16], gives $t_0 = 1.92$ eV. Fig. 5 shows the changes in the ground state as a function of u.

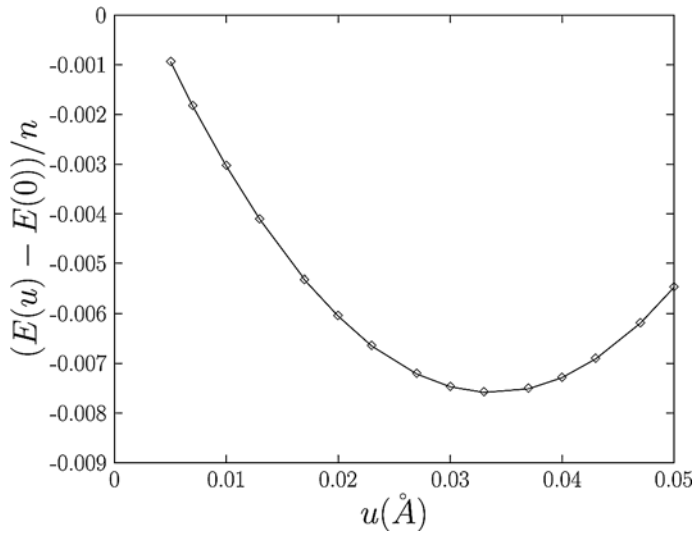

Fig. 5 – The ground state energy of boron-carbon hydrid chain (n = 12) as a function of the conjugation parameter u calculated at MP2 and DZ basis set level of theory (a.u.).

2. We fitted this ground state energy to Eq. 2 and found that $\alpha = 2.9$ eV/Å and $K = 14.8$ eV/(Å)^2. Substituting these parameters back into the SSH model and minimizing the ground state energy in terms of u using the perturbation theory dependent method [17] we obtain the ground state energy of π electrons

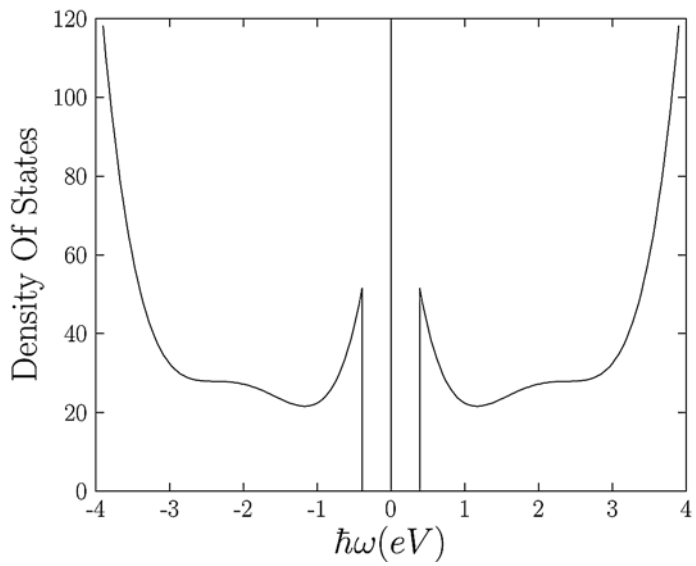

Fig. 6 – The density states of boron-carbon hydrid chain (n = 12).

and the corresponding density of states (DOS) as plotted in Fig. 6. The DOS shows a band gap of 0.8 eV at the Fermi level caused by the conjugation indicating that the one dimensional boron-carbon-hydrogen chain has a semiconductor character.

4. CONCLUSION

We performed an *ab initio* calculation on both boron-carbon and boron-carbon hydride chains. The final ground state energies and the geometrical configuration of both chains are obtained. The $(BC)_n$ chains are found to be not stable as one dimensional structure transforming into a two dimensional one. This structure could be considered as two interacting chains of boron and carbon or unfolded two ring of BC tubes. These chains are stabilized by adding hydrogen atoms to B and C atoms. The binding energy and Mulliken population of p_z-type orbital for both chains are calculated using HF-SCF theory and 3-21G basis set. These results can be approved by using MP2 theory and DZ basis set. The ground state energy $E(u)$ (eq., $n = 12$) in terms of the conjugation parameter u were determined by *ab initio* calculations at MP2 and DZ basis set. The conjugation of the $(HBCH)_n$ chain induces a gap of 0.8 eV at Fermi level which is less than the band gap of Silicon. This could lead to new applications in the area of semiconductors.

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