Computational study of carbon nanotube-substituted boron-nitrogen for hydrogen storage with density functional theory method (DFT)

K Anwar, R Gunawan*, R R D J N Subagyono
Chemistry Department, Faculty of Mathematics and Natural Sciences, Mulawarman University, Samarinda, East Kalimantan, Indonesia

*Corresponding author: e-mail: gunawan@fmipa.unmul.ac.id

Abstract. Computational study of pure carbon nanotube, carbon nanotubes and carbon nanotube substituted boron boron-nitrogen substituted as hydrogen storage has been done. This research was conducted using the method Density functional theory (DFT), B3LYP functional and basis set STO-3G. Substitution of boron and nitrogen atoms produce structures with lower total energy, while the boron atom substitution produces structures with higher total energy than the pure carbon nanotubes. Lowest total energy possessed by a carbon nanotube boron-nitrogen substituted by -1321 10^-14 J, while nanotube pure carbon structure of -1.319 10^-14 J and boron-substituted carbon nanotube of -1.314 10^-14 J. The total value of lowest energy is obtained from 105 structure with the addition of molecular hydrogen.

1. Introduction
One alternative energy source that has been attracting much attention at the moment is hydrogen fuel cells. As an energy conversion technology, hydrogen is highly efficient because it has a high thermal efficiency. Hydrogen fuel cell is also environmentally friendly because it has low emission and it is potential to be applied in the future [1].

Hydrogen storage systems by adsorption on the porous material technology has attracted the attention of many researchers. Carbon nanotubes (CNT) is a good storage material that has a good ability to adsorb hydrogen gas due to the large surface area and pore volume. Carbon nanotubes substituted with B or N atoms have a similar periodic structure that results from bonds of different structures from zigzag carbon nanotubes. When carbon atoms in carbon nanotube tubes are substituted with more nitrogen atoms, especially if the nitrogen atom occupies the same hexagonal structure, the excess electrons will interact and the structure will have different characteristics [2].

The substitution of carbon atoms in CNT with heteroatom such as nitrogen or boron provides a change in the nature, structural and electronic properties of CNT. Furthermore, the heteroatoms do not only change the physical properties of CNT, but also results in the unique properties [3].

Carbon nanotubes are a chain of carbon atoms bonded to each other in a non-solid hexagonal (hexagonal) tube that has a diameter of 1-2 nanometers with a single wall or more tube walls in sizes that vary from 1 nanometer to 100 nanometers in size. The length of the tube can reach sizes in the micrometer to centimeter range [4]. DFT does not do calculations based on the number of atoms of a molecule, but based on the electron density of a molecule, so the number of atoms will not affect the results of calculating the energy of the molecular optimization, this is very different from the results of
calculations using Molecular Mechanics, where Molecular Mechanics cannot explain the role of electrons in breaking and connecting bonds in a reaction [5].

Hydrogen adsorption capacity in carbon nanotubes is influenced by many factors such as the number of carbon nanotube walls (single wall or multi wall), purity, outer diameter, surface area, micropore volume, total pore volume, and pore size distribution. Small and uniform microporous volumes, minimal macroporosity, and high conductivity make single walled nanotubes (SWNT) have good potential as material for hydrogen storage. SWNT can adsorb hydrogen on the pore surface and the gap between SWNT stacks [6].

This paper reports computational studies on carbon nanotube substituted with Boron and Nitrogen atoms as material for hydrogen storage. The effect of substitution of boron and nitrogen on the structure of carbon nanotube is also described.

2. Computational Method
The computational study was conducted using the High Performance Computational Chemistry Software (NWChem). The method used was Density Functional Theory (DFT) using B3LYP functional (Becke, 3-parameter, Lee-Yang-Parr). Geometry optimization was performed to the molecular structures of single walled carbon nanotubes (armchair type) and single walled carbon nanotubes substituted by boron and boron-nitrogen before and after addition of hydrogen atoms. The single point energy calculations were conducted to obtain the lowest total energy.

2.1. Device
The hardware used to perform all calculations in this study were Dell Computer Intel® Core™ i3-3240 CPU @ 3.40GHz 3.40 GHz, Installed Memory (RAM) 2 GB, system type 64-bit Operating System, x64-based processor. The software used were Avogadro, NWChem, JMOL and WebMO.

2.2. Research procedure
This study used a Single Walled Carbon Nanotube (CNT) as the basic structure of molecular hydrogen storage. The basic structure consisted of hexagonal carbons with molecular formula C_{96}H_{16}. Carbon atoms in CNT (4.4) were substituted by boron or boron-nitrogen so that there were 3 variations of carbon nanotube investigated in the study. The structural models created using Avogadro before geometry optimization were shown in Figure 1. The structures were optimized using NWChem program by STO-3G basis set. Then hydrogen molecules were then inserted into the optimized structures (Figure 2).

![Figure 1. (A) pure CNT (b) CNT-substituted Boron (c) CNT-substituted Boron-Nitrogen](image-url)
HOMO and LUMO values were calculated to determine the position of bonding and anti-bonding orbital, the electronic properties of molecules and the wavelength of the single walled carbon nanotube (CNT), B-CNT and BN-CNT. The wavelength was calculated by Planck formula as follows:

\[ E = \frac{hc}{\lambda} \]

Where
- \( E \): Photon Energy
- \( h \): The constant Planck
- \( c \): Light speed
- \( \lambda \): Wavelength

3. Results and Discussion

3.1. Structure Optimization of pure CNTs, B-CNT and BN-CNT

The bond lengths, angles and diameters of CNT, B-CNT and BN-CNT after geometry optimization are presented in Table 1.

| Table 1. Bond length, bond angle and diameter of CNT, B-CNT and BN-CNT |
|-----------------------------|-----------------------------|-----------------------------|
| **Pure CNT**                |                             |                             |
| Bond length (Å)             | Bond angle (°)              | Diameter (Å)                |
| C35-C34                     | 1.42                        | C36-C35-C34                 | 117.4          |
| C35-C36                     | 1.42                        | C34-C35-C50                 | 120.1          |
| C35-C40                     | 1.42                        | C50-C35-C36                 |                |
| B-CNT                       |                             |                             |
| Bond length (Å)             | Bond angle (°)              | Diameter (Å)                |
| B35-C34                     | 1.42                        | C36-C35-C34                 | 117.4          |
| B35-C36                     | 1.42                        | C34-C35-C50                 | 120.1          |
| B35-C40                     | 1.42                        | C50-C35-C36                 |                |
| BN-CNT                      |                             |                             |
| Bond length (Å)             | Bond angle (°)              | Diameter (Å)                |
| B40-C57                     | 1.52                        | C47-B40-C41                 | 118.0°         |
| B40-C41                     | 1.53                        | C41-B40-C39                 | 116.5°         |
| B40-C39                     | 1.52                        | C39-B40-C47                 | 116.9°         |
| N48-C47                     | 1.44                        | C47-C49-N48                 | 117.8°         |
| N48-C49                     | 1.46                        | C49-C33-N48                 | 119.0°         |
| N48-C33                     | 1.46                        | C33-C47-N48                 | 117.8°         |

(a) pure CNT with Hydrogen (b) CNT substituted Boron with Hydrogen (c) CNT Boron-nitrogen substituted with Hydrogen

Figure 2.
The average bond lengths of pure CNT and B-CNT were 1.42 Å while that of BN-CNT was 1.52 Å. The increase in bond length may be due to the addition of nitrogen atom that has a larger number of valence electrons than boron. The nitrogen atom tends to attract carbon atoms in CNT stronger than boron atoms, resulting in a shorter N-C bond length than BN-C length. The structures of CNT, B-CNT and BN-CNT after optimization are shown in Figure 3.

![Figure 3](image)

**Figure 3.** (A) pure CNTs (b) CNT-substituted Boron (c) CNT-substituted Boron-Nitrogen

### 3.2. Pure CNTs, B-CNT and BN-CNT with the addition of molecular hydrogen

The energy of CNT, B-CNT and BN-CNT after addition of hydrogen (multiples of 5) is shown in Figure 4. The lowest energy was obtained after addition of 105 hydrogen molecules. The lowest energy for CNT was $-1.3398 \times 10^{-14}$ J, for B-CNT was $-1.3455 \times 10^{-14}$ J, and for BN-CNT was $-1.3469 \times 10^{-14}$ J. Addition of more than 105 molecules of hydrogen resulted in an increase in energy which may indicate that the carbon nanotubes became unstable.

![Figure 4](image)

**Figure 4.** Addition of Hydrogen Molecule chart on CNT Variation

Substitution with boron and nitrogen also resulted in the decrease in energy when hydrogen molecules were introduced to the system. Substitution with nitrogen may provide excess of electrons in the carbon nanotube. The energy reduction is caused by the effect of adding other atoms substituted on was BN-CNT because of the substitution of boron and nitrogen atoms. The structural stability was indicated by the addition of a diameter and the transfer of electrons between nitrogen and boron atoms.
Addition of hydrogen molecules did not only result in changes in current energy but also resulted in changes in bond length, angle and diameter in pure and substituted carbon nanotubes (Table 2).

**Table 2.** Bond length, angle and diameter of the CNT materials with 105 H₂

| Bond length (Å) | Bond angle (°) | Diameter (Å) |
|-----------------|---------------|--------------|
| C35-C34         | 1.43          | C36-C35-C34  | 118.2  |
| C35-C36         | 1.46          | C34-C35-C50  | 118.8  |
| C35-C40         | 1.46          | C50-C35-C36  | 117.3  |

| Bond length (Å) | Bond angle (°) | Diameter (Å) |
|-----------------|---------------|--------------|
| B35-C34         | 1.53          | C36-C35-C34  | 116.4  |
| B35-C36         | 1.52          | C34-C35-C50  | 118.4  |
| B35-C40         | 1.52          | C50-C35-C36  | 116.8  |

| Bond length (Å) | Bond angle (°) | Diameter (Å) |
|-----------------|---------------|--------------|
| B40-C57         | 1.53          | C57-B40-C41  | 118.6  |
| B40-C41         | 1.53          | C41-B40-C39  | 116.3  |
| B40-C39         | 1.52          | C39-B40-C57  | 116.6  |
| N48-C47         | 1.44          | C47-C49-N48  | 117.3  |
| N48-C49         | 1.45          | C49-C33-N48  | 119.0  |
| N48-C33         | 1.45          | C33-C47-N48  | 117.5  |

Based on Table 2, it can be seen that the longest bonds were the B-C bonds in BN-CNT with an average of 1.53 Å while the shortest bonds were the bond between N-C in BN-CNT with an average of 1.44 Å. Addition of hydrogens did not only result in differences in bond length but also affected the diameter of pure and substituted carbon nanotubes. The increase in diameter length was may be due to the interaction between hydrogen molecules in the carbon nanotubes (Figure 5).

![Figure 5](image)

**Figure 5.** (A) pure CNTs (b) CNT-substituted Boron (c) CNT-substituted Boron-Nitrogen with 105 H₂ molecules.

3.3. *HOMO & LUMO*

Energy calculations of HOMO and LUMO may help to understand the electron activity in CNT materials (Table 3). The presence of electron activities indicates that chemical interactions occur, a phenomenon in which systems consisting of atomic nuclei and electrons change, both in geometric
configuration and composition, including bonding and anti-bonding forces which are also caused by electrons [8].

Table 3. LUMO and HOMO Energies of CNT materials

|                  | Pure CNT       | B-CNT         | BN-CNT         |
|------------------|----------------|---------------|---------------|
| Energy (HOMO)    | -28 595 eV     | -24 906 eV    | -27 008 eV    |
| Energy (LUMO)    | -23 619 eV     | -18 077 eV    | -19 366 eV    |
| $E_{LUMO}-E_{HOMO}$ | 4976 eV        | 6829 eV       | 7642 eV       |
| Conversion to Joule | 7.97 x 10-19 J | 1.09 x 10-18 J | 1.22 x 10-18 J |
| Wavelength       | 255 nm         | 182 nm        | 163 nm        |

4. Conclusion
The substitution of carbon atoms with boron and nitrogen atoms resulted in changes in bond length, angle, and total energy. The pure carbon nanotubes and carbon nanotubes substituted with boron and boron-nitrogen had the same optimum storage capacity of 105 hydrogen molecules.

References

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