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# Boron-Substituted Fullerenes—Can They be One of the Options for Hydrogen Storage?

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## ABSTRACT

The need for an activator for hydrogenation of carbon nanomaterials
is outlined. The positions at which boron atoms are substituted in the
fullerene network have been identified for easy hydrogenation.

*Key Words:*   Please supply.

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## INTRODUCTION

Hydrogen storage has been a subject of considerable interest in recent times.[1] Hydrogen adsorption on carbon substrate is currently being vigorously explored as one of the possible potential solutions for hydrogen storage. It appears that newly found carbon nanomaterials (carbon nanofibers, nanotubes, and fullerene) may show promising potential towards storage capacities for hydrogen. Various theoretical and experimental studies have been directed to understand the nature of hydrogen adsorption by carbon materials.[2–7] In a recent study Schimmel et al.[8] have shown that low-temperature adsorption of hydrogen on carbon materials is related to the surface area and that carbon nanotubes with relatively low accessible area do not take up hydrogen as much as the high surface area activated carbon.

A number of inelastic neutron scattering experiments have been carried out to identify the sites and the strength of bonding of hydrogen molecule with various types of carbon materials at low temperatures. These studies essentially consider the dynamics, especially the rotational features of the physisorbed hydrogen molecule either entrapped inside the $C_{60}$ network[9] or in the interstitial tunnels of the SWNT bundles.[10] These studies essentially lead to the conclusion that the binding strength of hydrogen molecule is almost the same for all kinds of carbon materials and that the magnitude of interaction is nearly around $5\,kJ/mol$. Against this background, the need for an activator for hydrogenation in carbon materials is realized, which should be easily hydridable than carbon and facilitate migration of the dissociated hydrogen to carbon surface (equipotential). While considering these aspects heteroatoms such as N, P, and S seem to be promising to behave as activators in heteroatom containing carbon materials for hydrogen storage application.[11] This communication examines boron-substituted fullerenes as one of the options for hydrogen activation.

## METHODOLOGY AND RESULTS

The purpose of this communication is to examine the effect of substitution of boron in fullerene network on hydrogen activation. The typical $C_{60}$ model has been chosen for the study and the hydrogen molecule is allowed to interact as shown in Fig. 1 for the substituted and the unsubstituted fullerene. The stability of the substituted fullerene plays a crucial role in hydrogenation reaction and they seem to be stable by showing the minimum energy difference between original $C_{60}$ and the substituted $C_{60}$ molecule.[12,13] Computations using Density Functional Theory (DFT) have been carried out on the optimized configuration obtained using Universal Force Field (UFF 1.02)
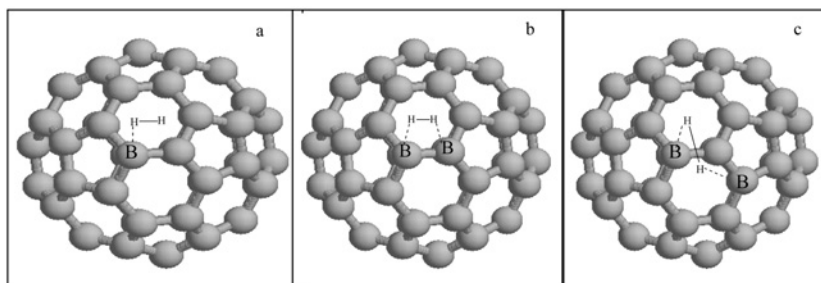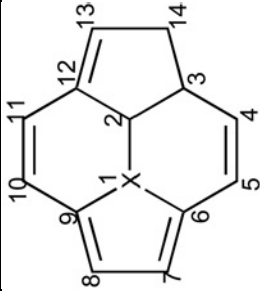
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**Figure 1.** Cluster model chosen for boron-substituted fullerene ($C_{60}$). (a) Single boron-substitution; (b) two boron-substituted in adjacent positions; (c) two boron-substituted in alternate positions.

parameter.[14] Cerius2 software was used for the force field calculations and the single point energy calculations on the optimized configurations obtained from force field have been carried out using Gaussian 98W[15] with Becke's three parameter hybrid function with LYP correlation function (B3LYP) and 6-31G(d) as basis set. The optimized geometrical parameters are given in Table 1. The results given in this Table show that the force field method is a reliable one. The total energy, H–H bond distance as well as the dissociation energy obtained from the single point calculations are given in Table 2. The points that emerge from the tabulated results are:

1. Substitution of carbon by boron atoms appears to favor the activation and dissociation of hydrogen molecule. The dissociation energy is decreased from 4.74 eV to 3.9 eV, when one boron is substituted and to 1.67 eV when two boron atoms are substituted in adjacent positions and to 0.3 eV when the two boron atoms are substituted in alternate positions.

2. H–H bond length also increased when hydrogen activation is carried out on boron-substituted fullerenes.

3. Boron-substituted in the alternate positions is more favorable than substitution at adjacent sites. This result is similar to what has been reported on boron-substituted carbon nanotubes. However, the bond length elongation is higher for the H–H bond in the case of the system where the boron atoms are substituted at adjacent positions.

The reasons for these observations have been examined by the calculation of transition state parameters, which show that the reaction proceeds from one

***Table 1.*** Geometrical parameters of the boron-substituted fullerene ($C_{60}$) molecule employing Universal Force Field parameters (UFF 1.02).



| Substitution | X-2 (Å) | X-6 (Å) | X-9 (Å) | 2-3 (Å) | 2-12 (Å) | 3-4 (Å) | <X-2-3 (deg) | <9-x-2-3 (deg) | <6-x-2-3 (deg) |
|---|---|---|---|---|---|---|---|---|---|
| $C_{60}$ | 1.400 | 1.400 | 1.420 | — | — | — | 108.1 | 0.0 | 0.0 |
| Single (X) | 1.656 | 1.589 | 1.580 | — | — | — | 116.4 | 7.1 | −7.3 |
| 2 'B' (adj) (X, 2) | 1.516 | 1.580 | 1.569 | 1.569 | 1.581 | — | 78.1 | 1.7 | 1.7 |
| 2 'B'' (alt) (X, 3) | 1.486 | 1.591 | 1.637 | 1.472 | 1.313 | 1.620 | 111.4 | 30.0 | −59.8 |

X = Single boron-substituted; X, 2 = Boron-substituted adjacent position; X, 3 = Boron-substituted alternate position.

***Table 2.***   Bond length and dissociation energy of hydrogen on the boron-substituted fullerene.

| S. no | Substitution | Total energy (a.u) | Bond length $H_1-H_2$ (Å) | Dissociation energy (eV) |
|-------|-------------|-------------------|---------------------------|--------------------------|
| 1 | Hydrogen | −1.175 | 0.708 | 4.740 |
| 2 | Unsubstituted fullerene | −2,286.042 | — | — |
| 3 | Unsubstituted fullerene + $H_2$ | −2,287.211 | 0.707 | 4.612 |
| 4 | 1 'B'-Substituted fullerene | −2,272.764 | — | — |
| 5 | 1 'B'-Substituted fullerene + $H_2$ | −2,273.908 | 0.818 | 3.918 |
| 6 | 2 'B'-Substituted fullerene (Adj) | −2,259.506 | — | — |
| 7 | 2 'B'-Substituted fullerene (Adj) + $H_2$ | −2,560.567 | 1.126 | 1.662 |
| 8 | 2 'B'-Substituted fullerene (Alt) | −2,259.487 | — | — |
| 9 | 2 'B'-Substituted fullerene (Alt) + $H_2$ | −2,260.477 | 1.016 | 0.276 |
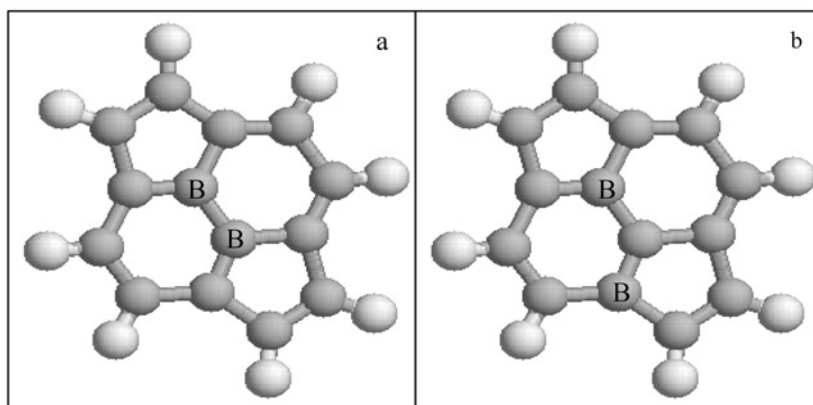


\* Where B= boron atom

***Figure 2.***   The optimized simple cluster model considered for the mechanistic pathway study. (a) Two boron-substituted in adjacent positions; (b)two boron-substituted in alternate positions.

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**Table 3.** Geometrical parameters of the simple cluster considered for the mechanistic pathway employing hybrid density functional B3LYP method with 6-31 g (d) basis set.
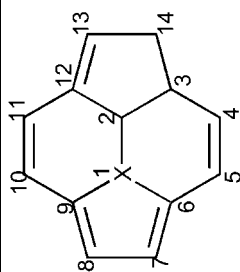


| Cluster | X-2 (Å) | X-6 (Å) | X-9 (Å) | 2-3 (Å) | 2-12 (Å) | 3-4 (Å) | <X-2-3 (deg) | <9-x-2-3 (deg) | <6-x-2-3 (deg) |
|---|---|---|---|---|---|---|---|---|---|
| $C_{60}$ | 1.400 | 1.400 | 1.420 | — | — | — | 120.0 | 0.0 | 0.0 |
| Unsub cluster | 1.352 | 1.431 | 1.431 | — | — | — | 122.6 | 0.0 | 0.0 |
| 2 'B' (adj) | 1.568 | 1.509 | 1.509 | 1.509 | 1.509 | 1.483 | 121.4 | 0.0 | 0.0 |
| 2 'B'' (alt) | 1.453 | 1.571 | 1.527 | 1.527 | 1.395 | 1.566 | 113.7 | −16.1 | −15.4 |

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*Where X = boron atom.

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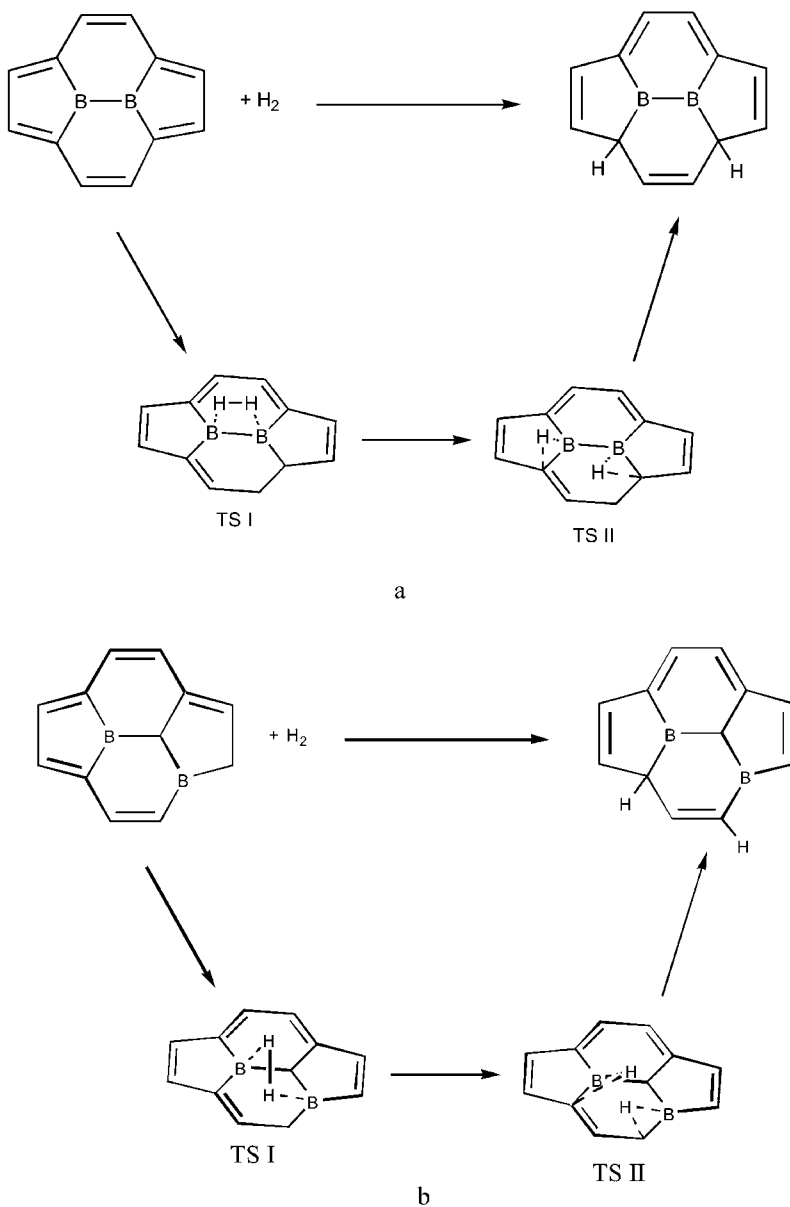


**Figure 3.**    The proposed mechanism of hydrogenation of boron-substituted fullerene. (a) Two boron-substituted in adjacent positions; (b) two boron-substituted in alternate positions.

**Table 4.**    The transition state optimized parameters of the cluster and the value of the activation energy.



| Substitution | $E_aI$ (eV) | $H_1$-$H_2$ (Å) | $B_1$-$H_1$ (Å) | $B_2$-$H_2$ (Å) | C-$H_1$* (Å) | C-$H_2$* (Å) |
|---|---|---|---|---|---|---|
| Adjacent (X, 2) | 2.26 | 1.98 | 1.19 | 1.29 | 2.52 ($C_6$) | 1.43 ($C_3$) |
| Alternate (X, 3) | 0.5 | 2.95 | 1.27 | 1.23 | 1.25 ($C_6$) | 1.97 ($C_4$) |

$Ea = TE$ (transition state) $-$ TE (reactant).

*, Shortest C$-$H bond distance.
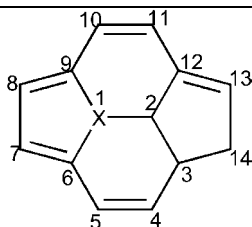
energy minimum to another via an intermediate maximum. From the transition state configuration one can predict the feasibility of the reaction. The hydrogen movement from the heteroatom can be conceived by the transition state theory calculation. Using the calculated property of transition state, the activation energy for the reaction is evaluated. To study the reaction mechanism of hydrogenation of boron-substituted fullerene, a simpler cluster model (Fig. 2) of pyracyclene ring structure has been taken, which is the subunit of $C_{60}$ molecule consisting of two pentagons and two hexagons and shows fulvalene-like character and is responsible for the facile reaction taking place in the fullerene molecule. The geometrical parameters of the cluster used for proposing the mechanism are listed in Table 3 and are similar to that of fullerene molecule ($C_{60}$). The ends of the cluster were saturated with hydrogen in order to avoid the edge effect[16] and the simple cluster selected in the present study, was fully optimized with hybrid density functional B3LYP method with 6-31G(d) basis set. The nature of stationary points thus obtained was characterized by frequency calculations. All the transition states corresponding to hydrogen migration were located and characterized as saddle points using the frequency calculations and were found to possess one imaginary frequency at the same levels of theory. The geometric parameters and the nature of the imaginary frequencies were examined using the graphical interface program, GaussView 03. The optimized geometrical parameters obtained from DFT calculations are given in Table 3.

Essentially the hydrogen activation and subsequent hydrogenation of carbon atoms of fullerenes are conceived by the pathways shown in Fig. 3.

In the alternate substitution configuration, the overall activation barrier is considerably reduced to nearly 0.5 eV, whereas for the situation of substitution at adjacent positions the activation barrier is of the order of 2.26 eV. This is an indication that substitution at alternate position is geometrically favorable for the hydrogenation of carbon atoms of fullerenes, while the hydrogenation of carbon is not that favourable for the system where boron is substituted in adjacent positions. The results substantiating these statements are given in Table 4.

These studies thus show that hydrogenation of carbon materials (carbon nanotubes or fullerenes) requires activation centers. Geometrically and chemically these activation sites have to be incorporated in the carbon network for effective hydrogenation.

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