



## NOTE

### Influence of Boron as a Heteroatom on Six Membered Borabenzenes

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Boron is an important bridge between classic inorganic and organic chemistry. The heterocycle derivatives of boron are used extensively in synthesis, the effort on investigation of these compounds can be pioneer. In this research, an *ab Initio* method by using 6-31G+ basis set was applied to consider the influence of boron atoms on stability and aromaticity character of some borinine compared with benzene.

**Key Words:** Borinine, Benzene, *Ab initio*, 6-31+G, Total energy, Aromaticity character.

Boron chemistry is widespread and this element is an important bridge between classic inorganic and organic chemistry. By combination with its neighboring elements in the periodic table boron results in an important number of molecules. The acidic tricoordinated  $sp^2$  boron atom coordinates to organic compounds bearing lone pairs. Boron coordination transforms the structure of organic molecules, as for example neutralizing the basic centers or forming heterocycles. It also changes the physicochemical properties of the ligand as in solubility or reactivity. For a given reaction, many different compounds can be formed by changing only the reaction conditions or the reagents ratio<sup>1</sup>.

The importance of boron reagents in modern organic synthesis is reflected in an increasing number of large scale applications of boron and its derivatives<sup>2</sup>.

As the heterocycle derivatives of boron are used extensively in synthesis, the effort on investigation of these compounds can be pioneer. The heterocyclic derivatives of boron show related patterns of reactivity have found considerable application in synthesis unlike lithium compounds, they are generally fairly stable to air and water but will undergo a range of selective reactions under relatively mild conditions<sup>3</sup>.

Carboranes are another boron derivatives, which are 'three-dimensional aromatic' molecules and undergo electrophilic aromatic substitution reactions not unlike traditional arenes. As in the case of aromatic organic molecules, substitution occurs at regiospecific locations on the cage<sup>4</sup>.

One of the interesting topics about boron compounds is their structures. In these compounds coordination fixes the configuration at the boron atom and at the coordinating

heteroatom. These configurations and even those of the neighbouring atoms can be assigned by NMR, thus boron functions as a stereochemical probe. Some examples where boron and nitrogen atoms are tetracoordinated stereogenic centers of stable configuration have been reported<sup>5,6</sup>.

In the study of dynamic systems such as inversion of atomic configuration, helixes interconversion, conformational and tautomeric equilibria, hydrogen bonding, *etc.* boron coordination plays an important role in freezing these processes, trapping conformers or tautomers or fixing the inversion of the configuration in labile atoms<sup>7,8</sup>.

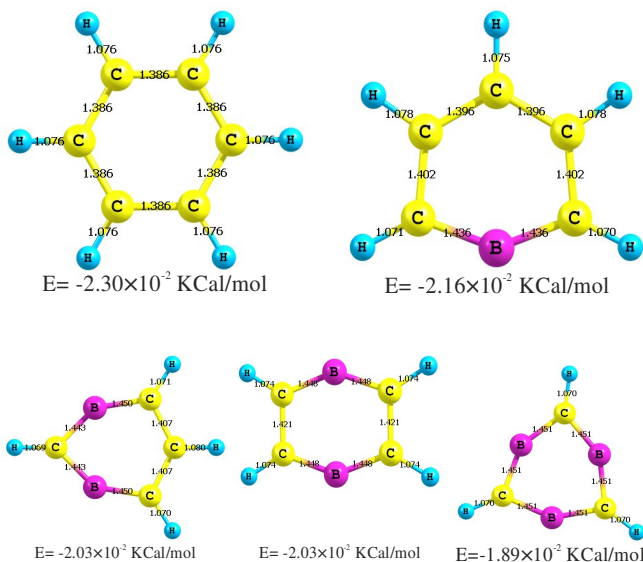
In heterocycles borane coordination promotes ring opening and alkylation of amines<sup>9-11</sup>. It also provides information on the basic sites and electron density distribution in organic molecules<sup>8,12</sup>. Borabenzenes have never been isolated because they are very strong Lewis acids<sup>13</sup>.

Although boron heterocyclic chemistry is not extensively developed yet it has a large potential<sup>14</sup>. Herein the stability of some borinine has been compared with benzene by an *ab initio* study and their optimized geometry and also their aromaticity character have been studied.

The molecular structures of borinine shown in **Scheme-I** are studied using *ab initio* method. Geometry optimizations are carried out by HF method using 6-31+G basis set of pc gamess version 7-1E<sup>15</sup> running on windows XP workstation in Pentium IV pc.

In \$data section scftyp and runtyp commands were performed RHF and optimize respectively. The latter command requests that a geometry optimization be performed. The geometry will be adjusted until a stationary point on the

potential surface is found. In \$basis section the basis set were described as:  $G_{\text{basis}} = \text{N31}$ ,  $N_{\text{gauss}} = 6$ ,  $N_{\text{dfunc}} = 1$ . The Cartesian format of molecular structure was described in \$data which was obtained from winmopac version 2. All the gamess outputs were opened by chemcraft software version 1.6.



Scheme-I. Optimized structures (6-31+G level)

Herein the six membered borinine and benzene ring were optimized *via ab initio* method by using 6-31+G basis set.

As the results show by comparing these six membered rings, introducing boron atom on benzene decreases stability of the molecules, by increasing the number of boron atoms the symmetry of the structures (depending on the boron atom location) decreases too. increasing in the number of boron atoms has direct relationship with stability decreasing. It is suggested the presence of boron in the ring perturbed aromaticity and concluded stability decreasing. By comparing bond

lengths of these compounds with benzene ring, it is found that C-B bonds are longer than C-C bonds in benzene but the heterocycles has preserved their flat structure. Despite it is expected the empty orbitals of boron attract the  $\pi$  electrons of the ring but herein probably the electronegativity differences between carbon and boron is predominant and the electron density on carbon atoms near boron are the most, so these carbons are sufficient places for electrophilic attacks. The optimized structures are shown **Scheme-I**, bond distances and total energy (E) units are Å and KCal/mol respectively.

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