A computational investigation on the stability and properties of the various isomers of B$_7^-$ anion

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Abstract
In the present study, the stability of seven and six-membered isomers of B$_7^-$ anion were considered in the triplet and singlet states at the M062X/6-311+G(d,p) level of the theory. The frontier orbital energy and HOMO-LUMO gaps of these isomers were calculated. A vibrational analysis performed at each stationary point was confirmed as a minimum energy. Natural bond orbital (NBO) and quantum theory of atoms in molecules (QTAIM) analyses were employed for illustration of the B-B bonds in the most stable isomer of B$_7^-$ anion. Aromaticity of this structure was studied in terms of the calculated nucleus independent chemical shift (NICS) values.

Keywords: B$_7^-$ anion; photoelectron sepectrum (PES); nucleus independent chemical shift (NICS); quantum theory of atoms in molecules (QTAIM); natural bond analysis (NBO).

Introduction
Experimental and theoretical investigations have proved boron clusters B$_n$ and B$_n^-$ in the size range of $n$=3-16 to be planar or quasi-planar [1-4]. The planarity of these clusters is attributed to their multiple aromaticity/antiaromaticity [1,2]. B$_n$ and its anions were considered as a novel family of inorganic ligands in chemistry. B$_7^-$ cluster is a prompting and complex cluster among all the small boron clusters. The presence of three quite different isomers in its photoelectron spectra was reported [3]. Quasi-planar hexa- coordinated B in B$_7^-$ ($C_{6v}$ B@B$_6$) [3] is recognized in joint photoelectron spectroscopy (PES) and theoretical studies. In a study, B$_7$Au$_2^-$ mixed cluster was prepared and its electronic structure and chemical bonding using photoelectron spectroscopy and ab initio calculations was investigated [5]. In other investigation, impressive capacity of the B$_7^-$ and V$_2$B$_7$ clusters for CO$_2$ capture has been reported [6].

In the present work, seven and six-membered isomers of B$_7^-$ anion in the singlet and triplet states at the M062X/6-311+G (d,p) level of the theory was investigated. Natural bond orbital (NBO) and quantum theory of atoms in molecules (QTAIM) analyses were employed for illustration of the B-B bonds in the most stable isomer of B$_7^-$ anion.
B\textsubscript{7} anion. Nucleus independent chemical shift (NICS) values were used to study the aromaticity.

**Computational methods**

All calculations were conducted with the Gaussian 09 suite program [7]. The standard 6-311+G(d,p) basis set [8,9] was utilized in the calculations. Geometry optimization was performed utilizing the hybrid functional of Truhlar and Zhao (M06-2X) [10]. A vibrational analysis carried out at each stationary point was confirmed as a minimum energy. The population analysis was also conducted by the natural bond orbital method [11] at M062X/6-311+G(d,p) level of theory using NBO 6.0 program [12] under Gaussian 2009 program package.

The nucleus-independent chemical shift (NICS) index, defined as the negative value of absolutely magnetic shielded and being basically determined by the magnetic criterion of aromaticity, is probably the most widely used probe for the examination of aromatic’s chemical compound properties [13]. The NICS index calculations are made by implementing the Gauge independent atomic orbital (GIAO) [14] method at the same level of theory for optimization.

Quantum theory of atoms in molecules analysis (QTAIM) computations were performed with Multiwfn 3.7 software package [15,16]. QTAIM calculations were computed by using the basic sets of optimization and M06-2X method. Visualization of the photoelectron spectrum (PES) was plotted with Multiwfn 3.7 software package [15].

**Result and discussion**

**Energetic aspect**

The various optimized isomers of B\textsubscript{7} molecule in singlet and triplet states are shown in Figure 1. The absolute energy and relative energies of these molecules are listed in Table 1.

It is possible to indicate that seven-membered ring (D\textsubscript{7h} symmetry) has more stability in the triplet state in comparison to singlet state. Vibrational analysis reveals one degenerate imaginary frequency for D\textsubscript{7h} symmetry in singlet and triplet states. This vibration mode places at -450.7 cm\textsuperscript{-1} in triplet state and leads to puckered ring. On the other hand, vibrational analysis reveals one imaginary frequency for D\textsubscript{7h} symmetry in singlet state. This vibration mode places at -74.5 cm\textsuperscript{-1} and leads to puckered ring.

Optimization of the six-membered ring discovers that the two studied isomers of B\textsubscript{7} anion have D\textsubscript{2h} and C\textsubscript{2v} in state (Figure 1). Vibrational analysis identified one imaginary frequency for D\textsubscript{2h} symmetry. This vibration mode places at -300.9 cm\textsuperscript{-1} and belongs to B\textsubscript{3u} symmetry representation. This vibration distorts molecules and changes its point group to C\textsubscript{2v}. Stability of the molecule in the effect of distortion equals 11.00 kcal/mol.

Optimization of the six-membered ring leads to isomers of B\textsubscript{7} anion having D\textsubscript{6h} and C\textsubscript{6v} in triplet state (Figure 1). Vibrational analysis finds an imaginary frequency for D\textsubscript{6h} symmetry. The wavenumber of this vibration mode detects at -238.7 cm\textsuperscript{-1} and descends the point group from D\textsubscript{6h} to C\textsubscript{6v}. This vibration distorts molecules and stabilizes the molecule about 2.16 kcal/mol.

It can be observed that six-membered rings are more stable in comparison to seven-membered rings. The stability trend of the six-membered ring isomers is:

C\textsubscript{6v}(T) > C\textsubscript{2v}(S) > D\textsubscript{6h}(T) > D\textsubscript{2h} (s) > D\textsubscript{7h}(T) > D\textsubscript{7h}(S)

Therefore, C\textsubscript{6v} isomer in the triplet state is the most stable isomer.
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**Figure 1.** The structures of the six and seven-membered isomers of the B\(_{7}\)\(^{-}\) anion.

**Table 1.** Energy (a.u), relative energy (kcal/mol), frontier orbital energy and HOMO-LUMO gap (eV) values of the studied isomers of B\(_{7}\)\(^{-}\) at the M062X/6-311+G(d,p) level of theory.

|        | E     | ΔE   | E(HOMO) | E(LUMO) | Gap    |
|--------|-------|------|---------|---------|--------|
| triplet|       |      |         |         |        |
| D\(_{6h}\) (T)    | -173.7419 | 2.16 | -2.12   | 3.13    | 5.24   |
| C\(_{6v}\) (T)    | -173.7454 | 0.00 | -1.94   | 3.23    | 5.17   |
| D\(_{7h}\) (T)    | -173.6470 | 61.71| -0.87   | 1.17    | 2.03   |
| singlet|       |      |         |         |        |
| D\(_{2h}\) (S)    | -173.7256 | 12.42| -1.78   | 1.42    | 3.20   |
| C\(_{2v}\) (S)    | -173.7431 | 1.43 | -1.88   | 2.65    | 4.53   |
| D\(_{7h}\) (S)    | -173.5696 | 110.28| -1.54   | 1.39    | 2.94   |

**Molecular orbital analysis**

The frontier orbital energy and HOMO-LUMO gap values of the B\(_{7}\)\(^{-}\) anion in the singlet and triplet states for the studied isomers are calculated. The calculated values in the Table 1 show that distortion increases the stability of HOMO in the singlet state. In contrast, distortion decreases the stability of LUMO in the singlet state.

On the other hand, distortion decreases the stability of HOMO in the triplet state. In contrast, distortion increases the stability of LUMO in the triplet state.

It is also possible to find out that distortion increases the HOMO-LUMO gap value in the singlet state. This increasing is compatible with the principles of minimum energy (MEP), and maximum hardness (MHP), that is, while a conformer changes from the most stable to the less stable species in most cases, the energy increases, and the hardness decreases [17-21].

**Photoelectron spectrum**

Figure 2 exhibits the theoretical photoelectron spectrum (PES) of the
most stable isomer of B₇⁻ anion. The plotting of PES spectrum based on (generalized) Koopmans' theorem. It can be found that first peak is placed at 2.91 eV. This result is compatible with experimental values of this anion (2.85 eV) [3].

Figure 2. The theoretical spectrum of the most stable isomer of B₇⁻ anion

1. Aromaticity

Aromaticity of the result planar ring due to the influence of distortion of D₆h symmetry structure on the triplet sate is investigated by the computation of nucleus-independent chemical shift (NICS) values in the center and above of the ring (0.5-2.5 Å). The calculated NICS value is -11.37 ppm at center of ring. The corresponding values at the 0.5, 1.0, 1.5, 2.0 Å above of the ring center are -32.67, -18.81, -10.25, -6.09, -3.76 ppm, respectively. These values proves that the most negative value of NICS at 0.5 Å is above the center of ring. Therefore, the presence of π-aromaticity for the six-membered ring of the C₆v symmetry in the triplet sate is evidenced.

2. Natural bond orbital analysis

The NBO results indicate that within the most stable isomer of B₇⁻ (C₆v, triplet), the boron atoms have negative charges (-0.09191 and -0.44853 for basal and apical boron atoms). Therefore, apical boron atom carries more negative charge in comparison to basal boron atom.

The atomic electron configuration of boron atoms are:

Bbasal: [core] 2s^0 2p^1.80 2p^0.20
Baxial: [core] 2s^0.62 2p^2.79

The hybridization of the contribution of atomic orbital in each one of B-B bonds are:

σ (Bbasal-σ Bbasal) = 0.7071B (sp^1.45) B(basal)+ 0.7072 (sp^1.46) B(basal)

π (Bbasal-π Bbasal) = 0.7068 (p^99.99) B(basal) + 0.7074 (p^99.99) B(basal)

σ(Baxial-Bbasal) = 0.6279 (sp^4.85) B(basal)+ 0.7783 sp^2.01 B(axial)

It is demonstrated that the contribution of hybride orbitals of B(axial) is more than B(basal) in the Baxial-Bbasal bond.

Also, NBO analysis reveals that the strongest interaction in this isomer is σ (Bbasal-Baxial) → LP*(1) B′basal (Figure 3). The stabilization energy (E(2)) and off-diagonal elements’ (Fij) values associated with this interaction are 145.33 and 0.328 kcal/mol.

The sp^2 orbital hybridization composed of 2s, 2pₓ and 2pᵧ valence orbitals of Baxial atom forms six equivalent partial bonds with the periphery boron ligands, with the Baxial-Bbasal Wiberg bond index equal to...
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0.6416. On the other hand, Wiberg bond index of B\textsubscript{basal}-B\textsubscript{basal} bond is 1.2505. Therefore, B\textsubscript{basal}-B\textsubscript{basal} bonds are more covalent than B\textsubscript{axial}-B\textsubscript{basal} bonds. Also, it is obvious that larger Wiberg index of B\textsubscript{basal}-B\textsubscript{basal} bond in comparison to B\textsubscript{axial}-B\textsubscript{basal} bond leads to shorter B\textsubscript{basal}-B\textsubscript{basal} bond being compared to B\textsubscript{axial}-B\textsubscript{basal} bond.

\[\sigma (B_{\text{Basal}}-B_{\text{axial}})\]

\[LP^*(1) B'_{\text{Basal}}\]

**Figure 3.** The presentation of the NBOs correspond to the strongest interaction for the most stable isomer of B\textsubscript{7}\textsuperscript{−} anion

3. **QTAIM analysis**

QTAIM theory has been proved as a powerful method for exploring chemical bonds [22]. AIM theory uses novel descriptors, such as the electron-density distributions at the bond critical point (BCP), to provide a deep insight into the nature of chemical bond [23-25]. Molecular graph of the most stable isomer of B\textsubscript{7}\textsuperscript{−} anion is presented in Figure 4. The topological properties of BCPs, including the electron density \(\rho(B-B)\), the Laplacian of the electron density \(\nabla^2\rho(B-B)\), the total energy density \(E\), the components of total energy density (G: Lagrangian kinetic energy, V: Virial energy density) are listed in Table 2. These values show that the changing trend of electron density in BCPs of B\textsubscript{basal}-B\textsubscript{basal} are larger than B\textsubscript{axial}-B\textsubscript{basal}. Large values of \(\rho(B_{\text{basal}}-B_{\text{basal}})\) are the indications of relatively strong bonds comparing to B\textsubscript{axial}-B\textsubscript{basal}.

The negative values of \(\nabla^2\rho(rb)\) and \(E\) illustrate that the B-B bond belongs to strong covalent interaction.

One can also use the \(|V(r)|/G(r)|\) ratio as another useful description. These values show that \(|V(r)|/G(r) > 2\) for BCPs of BB bonds (2.5 and 3.3 for B\textsubscript{axial}-B\textsubscript{basal} and B\textsubscript{basal}-B\textsubscript{basal}). This identifies a “classical” covalent interaction for these bonds.

**Figure 4.** Molecular graph of the most stable isomer of B\textsubscript{7}\textsuperscript{−} anion

Figure 5 reveals shaded surface maps with projection of electron density, Laplacian of electron density and Lagrangian kinetic energy of the most stable isomer of B\textsubscript{7}\textsuperscript{−} anion in the basal plane of molecule.
(a) Electron density

(b) Laplacian of electron density
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(c) Lagrangian kinetic energy

Figure 5. Shaded surface maps with projection of (a) electron density, (b) Laplacian of electron density and (c) Lagrangian kinetic energy of the most stable isomer of $B_7^{-}$ at the M062X/6-311+G(d,p) level of theory.

Also, Laplacian bond order values of $B_{\text{axial}}-B_{\text{basal}}$ and $B_{\text{basal}}-B_{\text{basal}}$ are calculated (Table 2). LBO values are a definition of covalent bond order based on the Laplacian of electron density and fuzzy overlap space [26]. These values reveal the smaller bond order values for $B_{\text{axial}}-B_{\text{basal}}$ than $B_{\text{basal}}-B_{\text{basal}}$.

Table 2. QTAIM analysis results of the BCPs of $B_{\text{axial}}-B_{\text{basal}}$ and $B_{\text{basal}}-B_{\text{basal}}$ for the most stable isomer of $B_7^{-}$ at the M062X/6-311+G(d,p) level of theory.

| Bond               | $\rho$ (e.Å$^3$) | $\nabla^2\rho$ (e.Å$^5$) | $G$ (a.u) | $V$ (a.u) | $E$ (a.u) | LBO      |
|--------------------|-------------------|--------------------------|-----------|-----------|-----------|----------|
| $B_{\text{axial}}-B_{\text{basal}}$ | 0.1423            | -0.1457                  | 0.0680    | -0.1724   | -0.1044   | 0.353745 |
| $B_{\text{basal}}-B_{\text{basal}}$ | 0.1559            | -0.2672                  | 0.0519    | -0.1707   | -0.1187   | 0.878195 |

Conclusion
Theoretical study on the seven and six-membered isomers of $B_7^{-}$ anion in the triplet and singlet states at the M062X/6-311+G(d,p) level of theory reveals that $C_{6v}$ isomer in the triplet state is the most stable structure among the studied isomers. The comparison of HOMO-LUMO gap values demonstrates that if the distortion of planar structure increases, the energy increases as well, and HOMO-LUMO gap decreases. Therefore, principles of minimum energy (MEP) and maximum hardness (MHP) is observed in these isomers. The most negative NICS value at 0.5 Å above the center of the ring in the most stable isomer identifies $\pi$-aromaticity in this isomer. Based on the NBO analysis results, the strongest interaction in the most stable isomer is $\sigma (B_{\text{basal}}-B_{\text{axial}}) \rightarrow LP^*(1)$ interaction. The calculated parameters of QTAIM analysis ($\rho$, $\nabla^2\rho$, $E$, $|V(r)|/G(r)$ ratio) indicates
that the B-B bond belongs to a strong covalent interaction and $B_{\text{basal}}$-$B_{\text{basal}}$ bonds are relatively strong bonds in comparison to $B_{\text{axial}}$-$B_{\text{basal}}$.

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