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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, $B_7Au_2^-$ 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_2B_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

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B_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_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_{7h} symmetry) has more stability in the triplet state in comparison to singlet state. Vibrational analysis reveals one degenerate imaginary frequency for D_{7h} symmetry in singlet and triplet states. This vibration mode places at -450.7 cm^{-1} in triplet state and leads to puckered ring. On the other hand, vibrational analysis reveals one imaginary frequency for D_{7h} symmetry in singlet state. This vibration mode places at -74.5cm^{-1} and leads to puckered ring.

Optimization of the six-membered ring discovers that the two studied isomers of B_7^- anion have D_{2h} and C_{2v} in state (Figure 1). Vibrational analysis identified one imaginary frequency for D_{2h} symmetry. This vibration mode places at -300.9 cm^{-1} and belongs to B_{3u} symmetry representation. This vibration distorts molecules and changes its point group to C_{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_7^- anion having D_{6h} and C_{6v} in triplet state (Figure 1). Vibrational analysis finds an imaginary frequency for D_{6h} symmetry. The wavenumber of this vibration mode detects at -238.7 cm^{-1} and descends the point group from D_{6h} to C_{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:

$C_{6v}(T) > C_{2v}(S) > D_{6h}(T) > D_{2h}(s) > D_{7h}(T) > D_{7h}(S)$

Therefore, C_{6v} isomer in the triplet state is the most stable isomer.

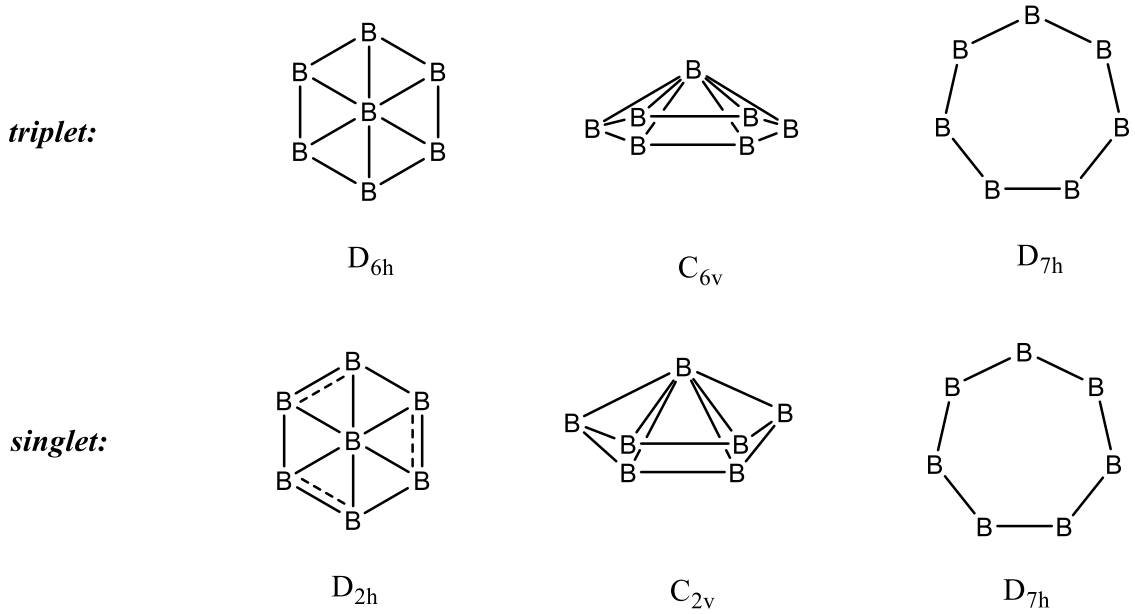


Figure 1. The structures of the six and seven-membered isomers of the B_7^- anion.

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 B_7^- 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].

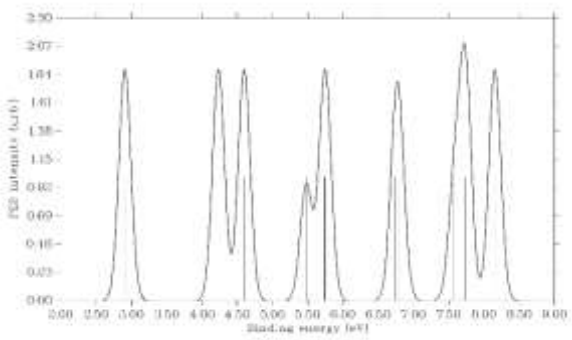


Figure 2. The theoretical spectrum of the most stable isomer of B_7^- anion

1. Aromaticity

Aromaticity of the result planar ring due to the influence of distortion of D_{6h} 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 C_{6v} symmetry in the triplet sate is evidenced.

2. Natural bond orbital analysis

The NBO results indicate that within the most stable isomer of B_7^- (C_{6v}, 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:

B_{basal}: [core] $2s^{0.89}\ 2p^{2.19}$

B_{axial}: [core] $2s^{0.62}\ 2p^{2.79}$

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

$\sigma\ (B_{basa\ l}\text{-}\ B_{basal}) = 0.7071B\ (sp^{1.45})_{B(basal)} + 0.7072\ (sp^{1.46})_{B(basal)}$

$\pi\ (B_{basal}\text{-}B_{basal}) = 0.7068\ (p^{99.99})_{B(basal)} + 0.7074\ (p^{99.99})_{B(basal)}$

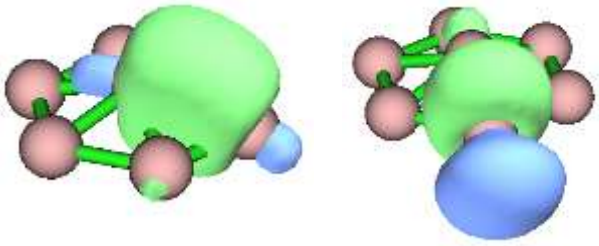
$\sigma(B_{axial}\text{-}B_{basal}) = 0.6279\ (sp^{4.85})_{B(basal)} + 0.7783\ sp^{2.01})_{B(axial)}$

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

Also, NBO analysis reveals that the strongest interaction in this isomer is $\sigma\ (B_{Basal}\text{-}B_{\ axial}) \rightarrow LP^*(1)\ B'_{Basal}$ (Figure 3). The stabilization energy ($E^{(2)}$)and off-diagonal elements' (F_{ij}) values associated with this interaction are 145.33 and 0.328 kcal/mol.

The sp^2 orbital hybridization composed of 2s, $2p_x$ and $2p_y$ valence orbitals of B_{axial} atom forms six equivalent partial bonds with the periphery boron ligands, with the B_{axial}-B_{basal} Wiberg bond index equal to

0.6416. On the other hand, Wiberg bond index of B_{basal}-B_{basal} bond is 1.2505. Therefore, B_{basal}-B_{basal} bonds are more covalent than B_{axial}-B_{basal} bonds. Also, it is obvious that larger Wiberg index of B_{basal}-B_{basal} bond in comparison to Baxial-B_{basal} bond leads to shorter B_{basal}-B_{basal} bond being compared to B_{axial}-B_{basal} bond.



σ (B_{Basal}-B $_{axial}$) LP*(1) B'$_{Basal}$

Figure 3. The presentation of the NBOs correspond to the strongest interaction for the most stable isomer of B_7^- 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_7^- anion is presented in Figure 4. The topological properties of BCPs, including the electron density ρ(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_{basal}-B_{basal} are larger than B_{axial}-B_{basal}. Large values of $\rho(B_{basal}$-$B_{basal})$ are the indications of relatively strong bonds comparing to B_{axial}-B_{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_{axial}-B_{basal} and B_{basal}-B_{basal}). This identifies a "classical" covalent interaction for these bonds.

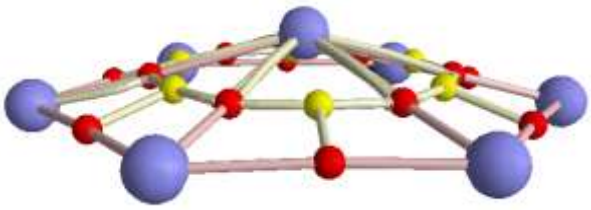
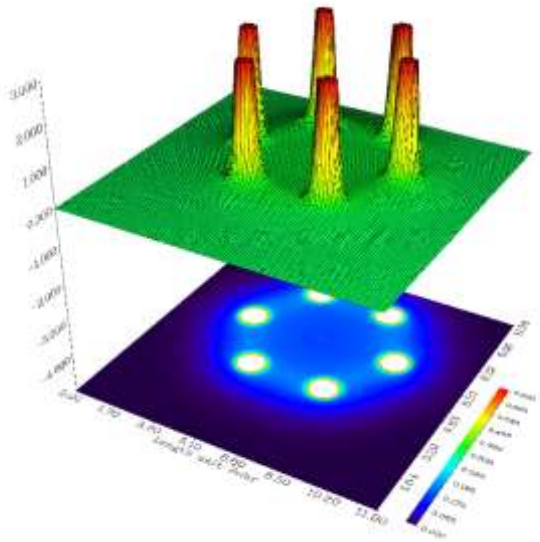
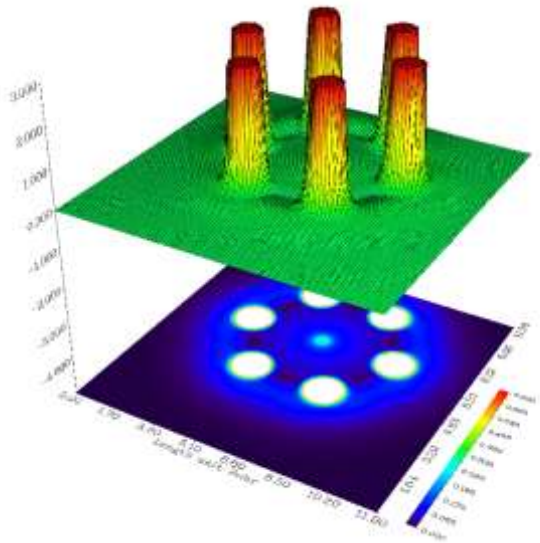


Figure 4. Molecular graph of the most stable isomer of B_7^- anion.

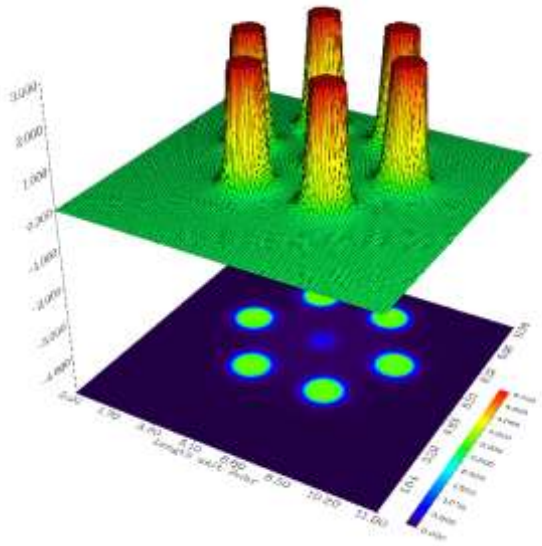
Figure 5 reveals shaded surface maps with projection of electron density, Laplacian of electron density and Lagrangian kinetic energy of the most stable isomer of B_7^- anion in the basal plane of molecule.



(a) Electron density



(b) Laplacian of electron density



(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^- anion in the basal plane of molecule

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

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

	ρ (e.Å^3)	**$\nabla^2\rho$(e.Å^5)**	**G(a.u)**	**V (a.u)**	**E (a.u)**	**LBO**
B_{axial}-B_{basal}	0.1423	-0.1457	0.0680	-0.1724	-0.1044	0.353745
B_{basal}-B_{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 the 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 π-aromaticity in this isomer. Based on the NBO analysis results, the strongest interaction in the most stable isomer is σ (B_{Basal}-B_{axial}) → LP*(1) interaction. The Calculated parameters of QTAIM analysis (ρ, $\nabla^2\rho$(rb), *E*, |V(r)|/G(r) ratio) indicates

that the B-B bond belongs to a strong covalent interaction and B_{basal}-B_{basal} bonds are relatively strong bonds in comparison to B_{axial}-B_{basal}.

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