# A B3LYP Study Searching for B-B Triple Bond in XBBX System
## (X= CO, CS, N$_2$, CNCH$_3$, H$_2$O, H$_2$S, NH$_3$, PH$_3$, C$_5$H$_5$N, F$^-$, CN$^-$, NO$_2$$^-$)

[1] Huimin Bi*, [1] Pengtao Xie, [1] Xingquan Chai, [1] Yan Liu, [1] Qing li and [2] Cuihong Sun

[1]*Handan key Laboratory of organic small molecule materials, Handan College, Hebei Handan 056002, China.*
[2]*College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang, 050016, China.*
binbi99@163.com*

**Summary:** A DFT study using B3LYP/6-311+G(3df,2p) method, has been performed to investigate the total energies, equilibrium geometries, bonding energies, and the values of spin contamination of BX and XBBX molecules, where X=CO, CS, N$_2$, CNCH$_3$, H$_2$O, H$_2$S, NH$_3$, PH$_3$, C$_5$H$_5$N, F$^-$, CN$^-$, NO$_2$$^-$. NBO analysis calculations also obtain the natural charges and bond orders at B3LYP/6-311+G(3df,2p) level. The quadruplet is ground state for both CO and CS ligands, by dimer of which can form stable singlet of XBBX. But for the remaining ligands, the doublets are ground states, contrary to the BCO and BCS systems.

Keywords: DFT B-B Triple Bond BX and XBBX molecules.

## Introduction

The boron, the only semimetal and three-center two electron (3c-2e) bonds, can easily react with small molecules such as CH$_4$, NH$_3$, C$_2$H$_2$, N$_2$, CO, H$_2$ to form new compounds, which have been explored by isolated matrix technique and photoelectron spectra [1, 2]. It has been reported a detailed study of the reactions of boron atoms and clusters with NO in solid argon to produce NBO, BBNO, BBBNO, OBNNO and BNBO [3]. Zhou and *et al.* have prepared several new boron carbonyls, BBCO, OCBBCO, and B$_4$(CO)$_2$ by the reactions of boron atoms or dimers with CO in a solid-argon matrix [4, 5]. The boron carbonyls exhibit intriguing structural and bonding properties. Combined matrix isolation infrared absorption spectroscopy and quantum chemical computations established OCBBCO to be a linear molecule with some boron-boron triple-bond character [3] [4]. Jones, Frenking, and Michalak [6-9], considering L→E≡E←L (E = B, Al, Ga, In) and (L = CO, CS, N$_2$, BO$^-$) systems, the NHC-stabilized L→B≡B←L compounds were predicted to be linear, and the distances of B-B is very short. Holger Braunschweig and *et al.* discussed some compound with a Boron-Boron triple bond [10].

Recently, the theoretical calculations propose the new idea that the BCO and CH are isolobal. Schleyer and *et al.* [11] explored similar relationships between polyhedral (BCO)$_n$ boron carbonyls and (CH)$_n$ hydrocarbon, and comparatively calculated (BCO)$_n$ and (CH)$_n$'s stable geometries and NICS values. Papaknodylis and *et al.* calculated the BX and YBBY molecules(X=He, Ne, Ar, Kr, CO, CS and N$_2$ [12]. They concluded that two $^4\Sigma^-$ B—Y moieties resulted singlet YB≡BY, similar to acetylene-like systems of $^1\Sigma_g^+$ symmetry. So if the boron-boron triple bond in the XBBX systems can form, Firstly, X, as ligand, must have lone-paired electrons, which can provide electrons to unoccupied p-block orbitals of boron. And then the ligand can contain the back donation of the boron p electrons to the ligand's orbital. Lastly, the quartet of the BX must be energetically more stable than the doublet. Based on above deduction, we connect boron molecule with different closed shell ligand, such as CO, CS, N$_2$, H$_2$O, NH$_3$, PH$_3$, F$^-$, CN$^-$, CNCH$_3$, in order to find the appropriate systems to form boron-boron triplet bonding. In this paper we report geometries, binding energies and values of spin contamination of BX and XBBX molecules, where X=CO, CS, N$_2$, CNCH$_3$, H$_2$O, H$_2$S, NH$_3$, PH$_3$, F$^-$, CN$^-$, C$_5$H$_5$N, NO$_2$$^-$. To be worth of comparision, we performed a systematically theoretical study on the the doublet and quartet of BX, and the singlet XBBX with density functional theory (DFT) method, which can describe boron systems well despite spin contamination [13, 14].

## Results and Discussions

We have investigated over twelve different ligands bonding to boron leading to doublet and quadruplet BX, whose two moieties form singlet XBBX(X= CO, CS, N$_2$, CNCH$_3$, H$_2$O, H$_2$S, NH$_3$, PH$_3$, C$_5$H$_5$N, CN$^-$, F$^-$, NO$_2$$^-$). Their bond characters are analysized on the basis of the natural charges, wiberg bond indices (WBI) values, bond lengths and bond dissociation energies.

Fig. 1 lists the NBO analysis, including the

---

*To whom all correspondence should be addressed.

natural charges and the wiberg bond indices(WBI) values for thirty different species at B3LYP/6-311+G(3df,2p) level. NBO analysis shows that the natural charge on boron of XBBX systems are even more negative than that of BX. It shows us the charges evidently transfer from ligands to boron. For CO, $H_2O$, $H_2S$, $NH_3$, $PH_3$, $CN^-$, $F^-$ ligands in XBBX systems, the wiberg bond indices(WBI) values of B-B are 2.260, 2.833, 2.235, 2.821, 2.403, 2.274, 2.793, respectively, while for CS, $N_2$, $C_5H_5N$, $NO_2^-$ ligands in XBBX systems, the WBI values of B-B are respectively 1.611, 1.887, 1.928 and 1.606, which are less than 2.000. For $CNCH_3$, the WBI value of B-B is even smaller, no more than 0.438,. We also obtain that the WBI value on boron-ligand in XBBX systems becomes smaller than that in BX systems.

The changes of natural charges and WBI values indicate that the electrons of ligands give the unoccupied p-block orbital of boron, which lead to the more negative charges on boron and smaller WBI values on boron-ligand in XBBX systems. The OCBBCO species has been discussed in previous results [5a]. Now considering CS as a example, the bonding mechanism is predicted a strong electron transfer for CS to $2p_z$ orbital of boron, giving rise to a σ-bond, a back-bonding interaction in the π-system, as well as a stronger B-CS bond in the quadruplet than doublet. To explain assistantly the bonding mechanism, Fig. 2 depicts the HOMO down to the seventh valence molecular orbital from the HOMO. HOMO and HOMO-1 are doubly degenerate orbital, composed of p-orbital of boron. The two degenerate HOMO-2 and HOMO-3 are dominatingly C—S π orbitals. The C—S π orbitals and boron-p orbitals make up of the doubly degenerate HOMO-4 and HOMO-5 orbitals. Obviously the HOMO-6 and HOMO-7 are the C—S 9σ-orbital back-donating to $B_2$ $2\sigma_u$ and $3\sigma_g$ orbitals, which are B—B antibonding and bonding character, separately.

Table 1-3 list total energies(corrected ZPE), spin contamination values, bond dissociation energies, the energy difference between doublet and quadruplet,

crucial bond lengths and bond angles of BX, where X=CO, CS, $N_2$, $CNCH_3$, $H_2O$, $H_2S$, $NH_3$, $PH_3$, $F^-$, $CN^-$, $C_5H_5N$, $NO_2^-$. All the calculations are calculated on the B3LYP/6-311+G(3df,2p) level. In general, when the ligands, CO, CS, $N_2$, $PH_3$, $CNCH_3$, $H_2O$, $H_2S$, $NH_3$, $F^-$ $CN^-$, $C_5H_5N$, and $NO_2^-$, bonding to boron, the bond distances of ligand will be elongated, which indicates that the bonds in ligands are weakened, consistent with the NBO analysis results. The bonding dissociation energies of doublet(18.6 kcal/mol, 55.8 kcal/mol) are much lower 8.2 kcal/mol and 12.3 kcal/mol than those of quadruplet(26.8 kcal/mol, 68.1 kcal/mol) for BCO and BCS. But for the other ligands, the bonding dissociation energies of doublet are higher than those of quadruplet. Even for $H_2O$, $H_2S$, $NH_3$, $CNCH_3$, and $NO_2^-$ ligands, the bonding dissociation energies of quadruplet are negative, which indicate the quadruplets are not stable. Seen from our calculations, when boron connects $CNCH_3$, $H_2O$, $H_2S$, $NH_3$, $F^-$ ligands, the boron atoms and bonded atoms are non-planar, while they are coplanar for X=CO, CS, $N_2$, $PH_3$, $CN^-$, $C_5H_5N$, $NO_2^-$ in XBBX systems. In NNB—BNN and $^-$FB—BF$^-$, the shortest and the longest B—B bond distances are respectively 1.368Å and 1.520 Å, between which for the other species B—B bond distances are less than 1.5 Å. The B—B bonding energies are 144.0 kcal/mol, 132.7 kcal/mol, 127.4 kcal/mol, 56.0 kcal/mol, 73.7 kcal/mol, 108.4 kcal/mo, 103.3 kcal/mo, 133.5 kcal/mo, 82.7 kcal/mo, 5.1 kcal/mo, 145.8 kcal/mol for X= CO, CS, $N_2$, $CN^-$, $F^-$, $H_2O$, $H_2S$, $NH_3$, $PH_3$, $C_5H_5N$, $NO_2^-$, $CNCH_3$. At the same calculation level, the B—B bonding energy of $^-$FB—BF$^-$ is -31.6 kcal/mol, which implies its singlet is not stable. At B3LYP/6-311+G(3df,2p) level the XBBX molecules were calculated to have short B—B bond lengths, which range between 1.520 Å and 1.368 Å, significantly shorter than the B—B double bond experimental characterized(1.57 Å -1.59 Å). From above calculation results, except for CO ligand, only CS ligand, the quadruplet is more stable than doublet in BCS species, energetically. Similar with BCO, two dimmer of BCS can also form singlet SCBBCS.

Table-1: Optimized total energies (Hartree, corrected ZPE), bond lengths(Å) and bond angles(°) at B3LYP/6-311+G(3df,2p) level.

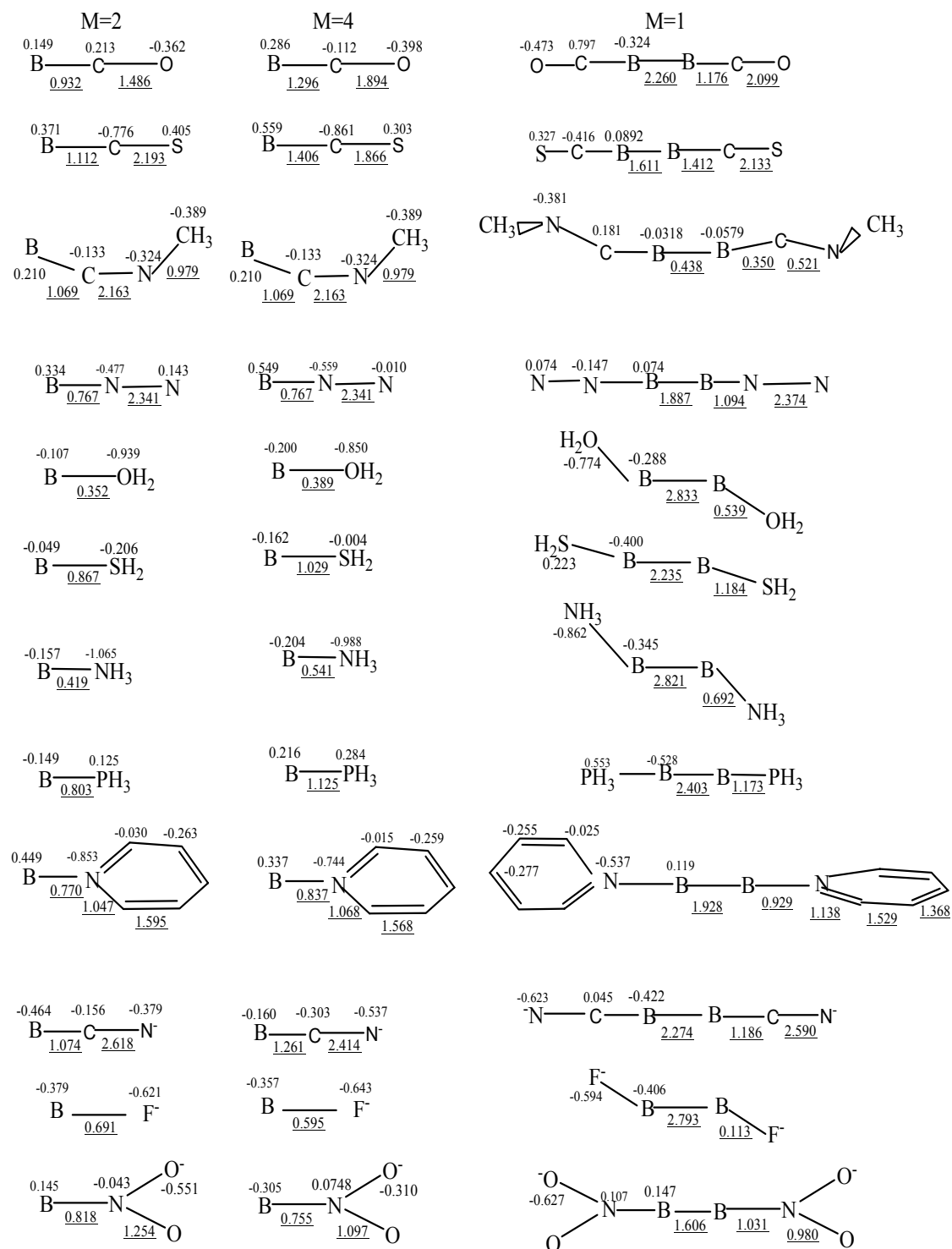| | CO | CS | NN | CN⁻ | F⁻ | OH₂ | SH₂ | NH₃ | PH₃ | C₅H₅N | NO₂⁻ | CNCH₃ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *E* | -113.351743 | -436.254446 | -109.561799 | -92.888656 | -99.888693 | -76.441956 | -399.413859 | -56.552631 | -343.154993 | -248.206916 | -205.228421 | -132.722597 |
| | $r_{B-C}$=1.125 | $r_{C-S}$=1.532 | $r_{N-N}$=1.091 | $r_{C-N}$=1.171 | | $r_{O-H}$=0.961 | $r_{S-H}$=1.341 | $r_{N-H}$=1.013 | $r_{P-H}$=1.417 | $r_{C-N}$=1.34 | $r_{N-O}$=1.254 | $r_{C-N}$=1.165 |
| | | | | | | ∡HOH= 105.2 | ∡HSH= 92.4 | ∡HNH= 111.6 | ∡HPH= 122.8 | ∡CNC= 1.398 | ∡ONO= 116.8 | 1.419 |

Fig. 1: The NBO analysis the natural charges and Wiberg bond index (WBI) values (underlined) of twelve different ligands at B3LYP/6-311+G (3df,2p) level.(M: Spin Multiply).
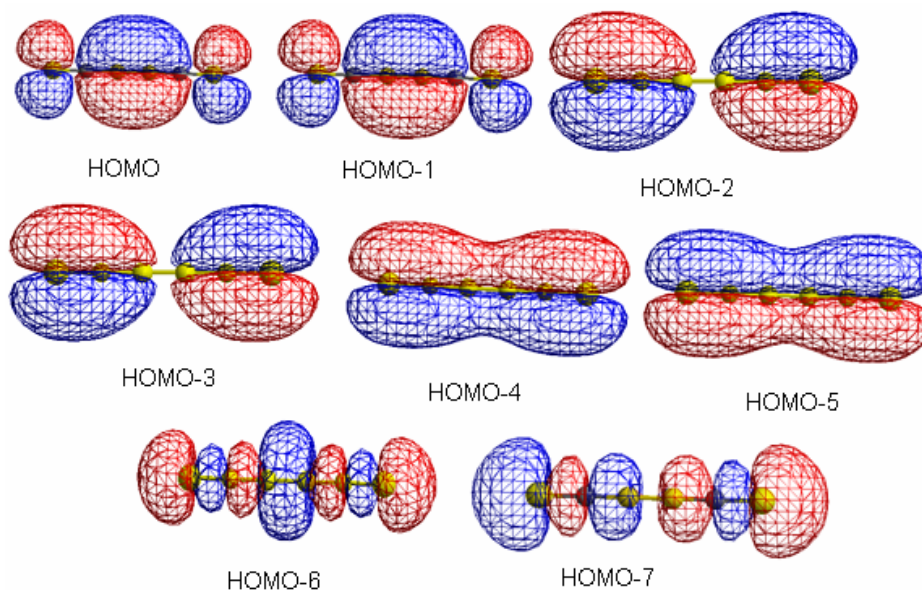
Fig. 2:    Molecular Orbital Pictures of Singlet SCBBCS.

Table 2:   Optimized total energies (Hartree, corrected ZPE), bond dissociation energies $D$e (kcal/mol), and bond distances (Å), bond angles (°) at B3LYP/6-311 + G (3df, 2p) level.

| | $B_2(CO)_2$ | $B_2(CS)_2$ | $B_2(NN)_2$ | $B_2(CN)_2^{2-}$ | $B_2F_2^{2-}$ | $B_2(OH_2)_2$ | $B_2(SH_2)_2$ | $B_2(NH_3)_2$ | $B_2(PH_3)_2$ | $B_2(NC_5H_5)_2$ | $B_2(NO_2)_2^{2-}$ | $B_2(CNCH_3)_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $E$ | -276.3434 | -922.26233 | -268.679596 | -235.37569 | -249.325046 | -202.345174 | -848.34926 | -162.634812 | -735.881607 | -546.017193 | -459.998461 | -315.114528 |
| $D_e{}^a$ | 144.0 | 132.7 | 127.4 | 56.0 | -31.6 | 73.7 | 108.4 | 103.3 | 133.5 | 82.7 | 5.1 | 145.8 |
| | $r_{B-B}$=1.444 | $r_{B-B}$=1.479 | $r_{B-B}$=1.368 | $r_{B-B}$=1.464 | $r_{B-B}$=1.520 | $r_{B-B}$=1.472 | $r_{B-B}$=1.433 | $r_{B-B}$=1.421 | $r_{B-B}$=1.433 | $r_{B-B}$=1.461 | $r_{B-B}$=1.498 | $r_{B-B}$=1.422 |
| | $r_{B-C}$=1.433 | $r_{B-C}$=1.411 | $r_{B-N}$=1.436 | $r_{B-C}$=1.486 | $r_{B-F}$=1.371 | $r_{B-O}$=1.543 | $r_{B-S}$=1.184 | $r_{B-N}$=1.543 | $r_{B-P}$=1.797 | $r_{B-N}$=1.427 | $r_{B-N}$=1.411 | $r_{B-C}$=1.422 |
| | $r_{C-O}$=1.148 | $r_{C-S}$=1.544 | $r_{N-N}$=1.129 | $r_{C-N}$=1.180 | | | $D_{SBBS}$=-103.7 | $D_{NBBN}$=178.8 | | | $r_{N-O}$=1.298 | $r_{C-N}$=1.198 |

$D_e{}^a$ adiabatically 2BX→XBBX

Table-3:  Optimized total energies(Hartree, corrected ZPE), values of spin contamination, bonding dissociation energies $D_e$ (kcal/mol), difference energies $T_e$(kcal/mol), bond distances(Å), bond angles(°) at the B3LYP/6-311+G(3df,2p) level.

| M = 2 | BCO | BCS | BNN | BCN⁻ | BF⁻ | BOH₂ | BSH₂ | BNH₃ | BPH₃ | BNC₅H₅ | BNO₂⁻ | BCNCH₃ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $E$ | -138.043813 | -461.005829 | -134.238246 | -117.643226 | -124.68772 | -101.113823 | -424.088286 | -81.235064 | -367.834449 | -272.94272 | -229.995142 | -157.441076 |
| $S2$ | 0.753 | 0.754 | 0.757 | 0.758 | 0.752 | 0.756 | 0.756 | 0.756 | 0.754 | 0.777 | 0.754 | 0.771 |
| $D_e$a | 18.6 | 55.8 | 8.8 | 57.8 | 85.7 | 5.9 | 7.5 | 12.5 | 10.7 | 46.0 | 65.4 | 35.2 |
| | $r_{B-C}$=1.602 | $r_{B-C}$=1.512 | $r_{B-N}$=1.453 | $r_{B-C}$=1.523 | $r_{B-F}$=1.325 | $r_{B-O}$=1.618 | $r_{B-S}$=1.920 | $r_{B-N}$=1.693 | $r_{B-P}$=2.067 | $r_{B-N}$=1.418 | $r_{B-N}$=1.427 | $r_{B-C}$=1.516 |
| | $r_{C-O}$=1.152 | $r_{C-S}$=1.547 | $r_{N-N}$=1.144 | $r_{C-N}$=1.179 | | $r_{O-H}$=0.971 | | | | $r_{N-C}$=1.413 | $r_{N-O}$=1.280 | $r_{C-N}$=1.202 |
| | | | | | | | | | | $r_{C-C}$=1.368 | | $r_{N-C}$=1.450 |
| | | | | | | | | | | | | ∠BCN=166.6 |
| | | | | | | | | | | | | ∠CNC=133.9 |
| | | | | | | | | | | | | DBCNC=8.4 |

| M=4 | BCO | BCS | BNN | BCN⁻ | BF⁻ | BOH₂ | BSH₂ | BNH₃ | BPH₃ | BNC₅H₅ | BNO₂⁻ | BCNCH₃ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $E$ | -138.056988 | -461.025447 | -134.23221 | -117.615142 | -124.586482 | -101.026405 | -424.041893 | -81.175149 | -367.814607 | -272.87895 | -229.873098 | -157.438048 |
| $S2$ | 3.756 | 3.764 | 3.782 | 3.770 | 3.752 | 3.751 | 3.755 | 3.751 | 3.753 | 3.784 | 3.769 | 3.763 |
| $D_e$a | 26.8 | 68.1 | 5.0 | 40.2 | 22.2 | -49.0 | -21.6 | -25.1 | -1.8 | 6.0 | -11.2 | 33.3 |
| $T_e$b | -8.3 | -12.3 | 3.8 | 17.6 | 63.5 | 54.9 | 29.1 | 37.6 | 12.5 | 40.0 | 76.6 | 1.90 |
| | $r_{B-C}$=1.408 | $r_{B-C}$=1.384 | $r_{B-N}$=1.453 | $r_{B-C}$=1.309 | $r_{B-F}$=1.381 | $r_{B-O}$=1.586 | $r_{B-S}$=1.760 | $r_{B-N}$=1.568 | 1.787 | $r_{B-N}$=1.417 | $r_{B-N}$=1.486 | $r_{B-C}$=1.401 |
| | $r_{C-O}$=1.166 | $r_{C-S}$=1.566 | $r_{N-N}$=1.144 | $r_{C-N}$=1.179 | | $r_{O-H}$=0.967 | | | | $r_{N-C}$=1.412 | $r_{N-O}$=1.329 | $r_{C-N}$=1.207 |
| | | | | | | | | | | $r_{C-C}$=1.372 | | $r_{N-C}$=1.425 |
| | | | | | | | | | | | | ∠BCN=175.5 |
| | | | | | | | | | | | | ∠CNC=146.4 |
| | | | | | | | | | | | | DBCNC=-180. |

$D_e$a   (²P)B+X→BX     $T_e$b energy difference of quadruplet and doublet

**Experimental**

All calculations are performed in the framework of GAUSSIAN 03 program package. We have carried out geometry optimization and vibrational frequency calculations at the B3LYP/6-311+G(3df,2p) level [15, 16]. For each structure, the stable method [17] has been used to establish a stable wavefunction. Different electronic states of the compounds have also been calculated to guarantee that the lowest electronic state is obtained in BX systems, where X=CO, CS, $N_2$, $CNCH_3$, $H_2O$, $H_2S$, $NH_3$, $PH_3$, $F^-$, $CN^-$, $C_5H_5N$, $NO_2^-$. NBO analyses are performed at the B3LYP/6-311+G(3df,2p) level to identify the bonding nature and intensities in these systems.

**Conclusions**

We have performed theoretical calculations for the BX and XBBX molecules, where X=CO, CS, $N_2$, $CNCH_3$, $C_5H_5N$, $H_2O$, $H_2S$, $NH_3$, $PH_3$, $F^-$, $CN^-$ and $NO_2^-$. The boron carbonyl compound BCO and OCBBCO have been characterized to have linear ground quadruplet and singlet state respectively by quantum chemical calculations. Other two electrons donors, CS , $N_2$ and $CN^-$, $PH_3$, $C_5H_5N$ , $NO_2^-$ can also bind to boron to form linear structures. The remaining $CNCH_3$, $H_2O$, $H_2S$, $NH_3$, $F^-$ ligands binding to boron can only form nonlinear compounds. According to our above discussions, only CS ligand can exhibit some boron-boron triplet bond character, which satisfies the octet rule.

So whether or not the boron-boron triple bond in the XBBX systems can form, there maybe need three fundamental conditions. Firstly, X, as ligand, must have lone-paired electrons, which can provide electrons to unoccupied p-block orbitals of boron. Latterly, and reversely, the ligand can contain the back donation of the boron p electrons to the ligand's orbital. Thirdly, the quartet of the BX must be energetically more stable than the doublet.

**References**

1. (a) G. H. Jeong, R. Boucher and K. J. Klabunde. *Journal of the American Chemical Society,* **112**, 3332 (1990). (b) P. Hassandadeh and L. Andrews. *Journal of the American Chemical Society,* **114**, 9239 (1992). (c) Y. Hannachi, P. Hassandadel and L. Andrews. *Journal of Physical Chemistry*, **98**, 6950 (1994). (d) Z. X. Wang and M. B. Huang. *Journal of the American Chemical Society*, **120**, 6758 (1998).

2. (a)T. J. Jr. Tague and L. Andrews. *Journal of the American Chemical Society*, **116**, 4970 (1994). (b) L. Andrews and X. F. Wang. *Journal of the American Chemical Society*, **124**, 7280 (2002).

3. M. Zhou, N. Tsumori, Q. Xu, G. P. Kushto and L. Andrews. *Journal of the American Chemical Society*, **125**, 11371 (2003).

4. M. Zhou, Q. Xu, Z. X. Wang and P. V. R. Schleyer. *Journal of the American Chemical Society,* **124**, 14854 (2002).

5. (a) M. Zhou, N. Tsumori, Z. Li, K. Fan, L. Andrews and Q. Xu. *Journal of the American Chemical Society,* **124**, 12936 (2002). (b) M. F. Zhou, Z. X. Wang, Schleyer P V R. and Xu Q. *ChemPhysChem.* **4**, 763 (2003).

6. L. C. Ducati, N. Takagi and G. Frenking, *Journal of Physical Chemistry.* A, **113**, 11693 (2009).

7. M. P. Mitoraj and A. Michalak, *Inorganic Chemistry.* **50**, 2168 (2011).

8. N. Holzmann, A. Stasch, C. Jones and G. Frenking, *Chemistry -A European Journal.* **17**, 13517 (2011).

9. S. D. Li, H. J. Zhai and L. S. Wang, *Journal of the American Chemical Society.* **130**, 2573 (2008).

10. H. Braunschweig, R. D. Dewhurst, K. Hammond, J. Mies, K. Radacki and A. Vargas, *Science.* 336, 1420 (2012).

11. H. S. Wu, H. Jiao, Z. X. Wang and P. V. R. Schleyer. *Journal of the American Chemical Society,* **125**, 4428 (2003).

12. A. Papakondylis, E. Milliordos and A. Mavridis. *Journal of Physical Chemistry* A*,* **108**, 4335 (2004).

13. T. D. Crawford, E. Kraka, J.E. Stanton and D. Cremer. *Journal of Chemical Physics,* **114**, 10638 (2001).

14. J. Grafenstein, A. M. Hjerpe, E. Kraka and D. Cremer. *Journal of Physical Chemistry* A*,* **104**, 1748 (2000).

15. A. D. Becke. *Journal of Chemical Physics,* **98**, 5648 (1993).

16. V. Esmail. *Journal of the Chemical Society of Pakistan*, **31**, 269 (2009).

17. R. Bauernschmitt and R. Ahlrichs, *Journal of Chemical Physics,* **104**, 9047 (1996).