



# Article Theoretical Insight into B–C Chemical Bonding in *Closo*-Borate $[B_nH_{n-1}CH_3]^{2-}$ (n = 6, 10, 12) and Monocarborane $[CB_nH_nCH_3]^{-}$ (n = 5, 9, 11) Anions

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**Abstract:** A theoretical investigation of mono-methyl derivatives of *closo*-borate anions of the general form  $[B_nH_nCH_3]^{2-}$  (n = 6, 10, 12) and monocarboranes  $[HCB_nH_nCH_3]^{-}$  (n = 5, 9, 11) was carried out. An analysis of the main bonding descriptors of *exo*-polyhedral B–C bonds was performed using the QTAIM (quantum theory of "Atoms in Molecules"), ELF (electron localisation function), NBOs (natural bond orbitals) analyses and several other approaches for the estimation of B–C bond orders (viz. Laplacian bond order (LBO), fuzzy bond order (FBO) and Mayer and Wiberg formalisms). Based on the data obtained on electron density descriptors, it can be concluded that orbital interaction increases with increasing boron cluster size. The present investigation provides a better understanding of *exo*-polyhedral B–C bond strength, which can be useful for studies devoted to the synthesis and properties of boron cluster systems.

Keywords: closo-borate; carborane; DFT; QTAIM; ELF; NBO; chemical bonding

## 1. Introduction

Molecular modelling is widely applied in modern inorganic chemistry [1–3]. Theoretical approaches make it possible to very accurately predict the relationship between the structure of a chemical substance and its properties [4]. This makes it possible to find the most promising molecular systems, even before they are obtained experimentally [5–7]. The most important characteristics of chemical systems, such as bonding, reactivity and spectroscopy, can be evaluated through theoretical investigation [8–10].

Chemical bonding is one of the central issues of theoretical chemistry [11–13]. Traditionally, methods based on molecular orbital and electron density properties are used [14–16]. The natural bond orbital (NBO) approach represents molecular orbitals in a Lewis-like bonding pattern of electron pairs [17,18]. Methods of the quantum theory of "Atoms in Molecules" (QTAIM) and electron localisation functions (ELFs) are actively used to study electron density distribution in chemical compounds [19–21]. These approaches make it possible to discover the main structure patterns of valence and non-valence contacts in a simple and clear form [22–24]. Another important characteristic of chemical systems is charge distribution [25]. In many cases, a given descriptor helps to find local reactivity centres [26,27].

The results of several experimental and theoretical research studies devoted to the chemistry of *closo*-borate anions and related compounds (carboranes, metalloboranes) have



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). already been published [28–34]. Interest in *closo*-borate compounds and their analogue carboranes and metalloboranes is motivated by the possible application of such molecular species in medicine, nonlinear optics, fluorescent materials, etc. [35–39]. Theoretical studies devoted to boron cluster anions have focused on the structure and chemical properties of relevant systems [40,41]. Such investigations provide a deeper understanding of the chemical nature of these compounds [42–44]. The main features of *exo*-polyhedral bonds B– X, where X = H, C, N and O, in *closo*-borate anions and related compounds were estimated with the help of the QTAIM method [45,46]. The main trends in exo-polyhedral bond strength as a function of the nature of the boron cluster were observed, and the same method has also made it possible to investigate the non-covalent contacts between boron clusters and organic molecules [47-50]. Based on the use of conceptual DFT methods, the most reactive molecular platforms in the series of boron *closo*-boron anions were found [51,52]. The electrophilicity index  $\omega$ , invented by Parr [53], and the related index  $\varepsilon$ , which was introduced by Syun-ichi Kiyooka et al. [54], are the most useful descriptors for estimating the electrophilic nature of molecules. Such theoretical studies have made it possible to find the most promising boron-containing systems for further functionalisation.

To date, the main descriptors of B–C bonds in derivatives of the general form  $[B_nH_{n-1}COR]^{2-}$ R = H, OH, CH<sub>3</sub>, OCH<sub>3</sub> and  $[B_nH_{n-1}CO]^-$  have been investigated [55,56]. The values of the main topological parameters for B–C interaction are typical for closed-shell dative bonding interactions. The authors have found that, for lengths of B–C bonds, the Wiberg index and topological descriptors of electron density, the main trends are the same not just for *closo*-borate anions, but also for N(CH<sub>3</sub>)<sub>3</sub>BH<sub>2</sub>COR. In the case of  $[B_nH_{n-1}COH]^{2-}$  (n = 6, 10, 12), the B–C bonds are the most stable, being supported by the highest value of electron density at the bonding critical point, larger delocalisation indices and d(B,C), indicating a higher degree of electron sharing between the boron atoms and the carbon atoms.

The study of *exo*-polyhedral B–C bonds is an interesting and crucial one, and needs to be expanded further. Understanding the nature of *exo*-polyhedral bonds has two purposes. On the one hand, it is of fundamental and theoretical interest. Investigating the nature of these chemical bonds allows one to identify features in the molecular orbitals, electronic distribution and bonding energies. On the other hand, the obtained knowledge can be used in the synthesis of the obtained compounds. In turn, the obtained compounds can have a number of useful properties and find practical applications. In the current work, it was decided to focus on methyl derivatives of *closo*-borate anions of the general form  $[B_nH_{n-1}CH_3]^{2-}$  (n = 6, 10, 12). These derivatives were chosen because they are the simplest model objects containing the desired chemical bonds. In addition, methyl derivatives of monocarboranes  $[CB_nH_nCH_3]^{2-}$  (n = 5, 9, 11) were selected. These systems were studied to enable an understanding of how the introduction of a heteroatom into the cluster cage affects the properties of *exo*-polyhedral bonds. Applying several bond descriptors, the phenomenon of *exo*-polyhedral B–C bonding in these compounds was studied.

#### 2. Results and Discussion

The main descriptors of chemical bonding in methylated derivatives of closo-borate anions of the general form  $[B_nH_{n-1}CH_3]^{2-}$  (n = 6, 10, 12) and monocarboranes  $[CB_nH_nCH_3]^-$ (n = 5, 9, 11) were explored. For ten vertex carboranes  $[HCB_{10}H_9CH_3]^-$ , only isomers with carbon atoms in an apical position were considered. This decision was made in order to provide a large number of all possible isomers. Consideration of all isomers would not, however, provide more information about the B–C bonding phenomenon. The results obtained for cluster systems were compared with analogous  $BH_{3-n}(CH_3)_n$  (n = 1–3) systems. The main bond descriptors of  $BH_{3-n}(CH_3)_n$  (n = 1–3) systems have been investigated in previous studies. This comparison provides more information on how *exo*-polyhedral bonds B–C differ from analogue systems with one boron atom. Optimised geometries of all model systems are shown in Figure 1. [B6H5CH3]<sup>2-</sup>

[1-B10H9CH3]<sup>2-</sup>

[ortho-CB<sub>5</sub>H<sub>5</sub>CH<sub>3</sub>]





**Figure 1.** Optimised structures of closo-borate anions of the general form  $[B_nH_{n-1}CH_3]^{2-}$  (n = 6, 10, 12), monocarboranes  $[CB_nH_nCH_3]^{-}$  (n = 5, 9, 11) and  $BH_{3-n}(CH_3)_n$  (n = 1–3).

The QTAIM, ELF and NBO approaches, as well as several others for estimating bond orders, were used. All of the approaches presented are reliable and have been proven in a multitude of works [16,57,58]. On the other hand, from time to time, there may be situations in which one or more methods may not show very good results [59,60].

Considering descriptors in aggregate and studying correlations between them allow us to find the most reliable descriptors of *exo*-polyhedral B–C bonds.

The analysis started with the calculation of B–C bond length. This parameter is the simplest to calculate, and estimating this parameter provides a good starting point for the following analysis and discussion. In most cases, this parameter is well-correlated with bond strength [61]. Bond order is also a simple and clear descriptor for bond analysis. Molecular orbitals involved in the formation of B–C bonds were analysed with the help of NBO formalism. The use of descriptors based on electron density for perception and interpretation is more complicated but can provide much information about electron distribution in molecules of particular interest. An analysis was made of how these approaches correlate with one another. A matrix of correlations is presented in Figure 2. These correlations enabled the most reliable descriptors to be found.



**Figure 2.** Correlation matrix of main B–C bond descriptors in closo-borate anions of the general form  $[B_nH_{n-1}CH_3]^{2-}$  (n = 6, 10, 12), monocarboranes  $[CB_nH_nCH_3]^{-}$  (n = 5, 9, 11) and  $BH_{3-n}(CH_3)_n$  (n = 1–3). For monocarboranes, only *exo*-polyhedral B–C bonds were considered.

As stated above, the simplest parameter to calculate is bond length. Thus, values of B–C bond lengths were estimated. As seen in Figure 3 and Table S2, calculated values lay in the narrow range 1.60–1.63 Å. In the case of monocarborane derivatives, bond lengths were shorter than those in closo-borate systems. Bond lengths of BH<sub>3-n</sub>(CH<sub>3</sub>)<sub>n</sub> (n = 1–3) were shorter than for cluster species, being in the range 1.56–1.58 Å. One can conclude that range of *exo*-polyhedral B–C bond values is very narrow. However, the use of other bond descriptors allows a more detailed analysis of the main differences between the studied classes of compounds.



**Figure 3.** Values of B–C bond lengths in closo-borate anions of the general form  $[B_nH_{n-1}CH_3]^{2-}$  (n = 6, 10, 12), monocarboranes  $[CB_nH_nCH_3]^-$  (n = 5, 9, 11) and  $BH_{3-n}(CH_3)_n$  (n = 1–3). For monocarboranes, only *exo*-polyhedral B–C bonds were considered.

Several approaches to B–C bond order analysis were used. Laplacian bond order (LBO), fuzzy bond order (FBO) and the Mayer and Wiberg approaches were applied (Table S2). The Wiberg bond order approach is based on application of the P matrix, where P is known as the density matrix [62]. The Wiberg bond order uses the square of the off-diagonal elements of density matrix P. In the present case, Wiberg bond order in the NAO basis was applied.

$$I_{AB} = \sum_{a \in A} \sum_{b \in B} P_{ab}^2$$

Mayer bond order can be seen as an extension of Wiberg bond order [63]. The Mayer bond order between atom A and B is defined as

$$I_{AB} = I_{AB}^{\alpha} + I_{AB}^{\beta} = 2\sum_{a \in A} \sum_{b \in B} [(P^{\alpha}S)_{ba}(P^{\alpha}S)_{ab} + (P^{\beta}S)_{ba}(P^{\beta}S)_{ab}]$$

where  $P^{\alpha}$  and  $P^{\beta}$  are the alpha and beta density matrix, respectively, and S is the overlap matrix.

Fuzzy bond order (FBO) was first proposed by Mayer [64].

$$B_{AB} = B_{AB}^{\alpha} + B_{AB}^{\beta} = 2\sum_{\mu} \sum_{\nu} [(P^{\alpha}S)_{\mu\nu} (P^{\alpha}S)_{\nu\mu} + (P^{\beta}S)_{\mu\nu} (P^{\beta}S)_{\nu\mu}]$$
$$S_{\mu\nu}^{A} = \int w_{A}(r) \chi_{\mu}^{*}(r) \chi_{\nu}^{*}(r) dr$$

where **S** is the overlap matrix of basis functions in fuzzy atomic spaces.

Laplacian bond order (LBO) is based on evaluation of  $\nabla^2 p$  in fuzzy overlap space [65].

$$L_{A,B} = -10 \times \int_{\nabla^2 p < 0} w_A(r) w_B(r) \nabla^2 p(r) dr$$

The criterion of reliability of these approaches was investigated through the correlation of other bond descriptors, such as bond length, and defined within QTAIM and ELF approaches. If the descriptor has good correlation with other descriptors, it can be described as the reliable descriptor for the B-C bond. The best results were obtained with LBO approaches. The correlation coefficient with bond length was equal to -0.98, with different QTAIM parameters lying in the range 0.89–0.96 (absolute values). The FBO analysis was not as good, but also gave reliable results. In this case, the correlation coefficient with bond length was equal to -0.92, with different QTAIM parameters lying in the range 0.80–0.84. In the Mayer analysis, some of the values for bond orders of closo-borate systems were unreliably small, being within the range 0.11–0.47. The Wiberg bond order correlated poorly with other bond descriptors, and bond lengths in particular. The correlation coefficient with bond length was -0.23, and with different QTAIM parameters, it lay in the range 0.29–0.34, in absolute values. The main issue with Wiberg bond order analysis in NAO was that these methods did not fit well for systems with the multi-centre bonding patterns. In the case of the Mayer approach, problems could arise from the application of the basis set with diffuse functions. However, LBO and FBO approaches were free from this disadvantage and gave quite reliable results. Thus, for the analysis of bond orders, the main focus was on LBO indices (Figure 4). In general,  $BH_{3-n}(CH_3)_n$  (n = 1–3) had the greatest bond order values among all considered systems. For cluster systems, mono-carborane anions had greater bond order values than closo-borate anions, with absolute values in the interval 0.95-1.01. For carborane systems with ortho-CH<sub>3</sub> group, the B–C bond order values were higher than for other isomers. For closo-borate anions, bond order values were in the range 0.89–0.92. Based on these results, it can be concluded that for a cluster system, there are no back-bonding effects whereby a carbon atom donates electron density to boron atoms, unlike in  $BH_{3-n}(CH_3)_n$  (n = 1–3) systems.



**Figure 4.** Values of B–C Laplacian bond orders in closo-borate anions of the general form  $[B_nH_{n-1}CH_3]^{2-}$  (n = 6, 10, 12), monocarboranes  $[CB_nH_nCH_3]^{-}$  (n = 5, 9, 11) and  $BH_{3-n}(CH_3)_n$  (n = 1–3). For monocarboranes, only *exo*-polyhedral B–C bonds were considered.

The main characteristics of B–C bonding orbitals were estimated, as was the value of the energy of the 2c–2e bonding molecular orbital that corresponded to the B–C bond (Figure 5 and Table S4). The estimation of B–C bonding orbitals was carried out with the help of NBO formalism.  $BH_{3-n}(CH_3)_n$  (n = 1–3) had more negative energy of the bonding orbital than cluster systems. For cluster systems, the value of the energy from the bonding orbital increased with increasing boron cluster size, and carborane systems had greater values than closo-borate systems. As in the case of bond orders, the bonding orbital energy of the carborane system with ortho- $CH_3$  group values was higher than for other isomers. Additionally, the contribution of the atomic orbital in the bonding molecular orbital was calculated. In all cases, orbitals of the C-atom had the largest atomic orbital contribution values. The percentage of carbon atom orbitals' contribution to the molecular orbital varied from 62 to 68%.  $BH_{3-n}(CH_3)_n$  (n = 1–3) species had the lowest values of boron atom contribution among all considered systems. Carborane anions had a greater value of boron atom contribution than closo-borate. The value of the contribution of the boron atom increased with increasing boron cluster size. In addition, the analysis of the back-bonding effect on the exo-polyhedral B-C bond was carried out with the help of second-order perturbation theory analysis of the Fock matrix in the NBO basis (Table S5). This effect is expressed as the donation of electrons from a C–H bond to a vacant electron orbital of a boron atom. The donor-acceptor stabilisation energy E(2) was estimated. In the case of  $BH_{3-n}(CH_3)_n$  (n = 1–3), the values of E(2) lay in the range of 1.95–7.23 kcal/mol. For closo-borate systems,  $[B_nH_{n-1}CH_3]^{2-}$  (n = 6, 10, 12) lay in the range of 0.05–0.15 kcal/mol. For carborane species, total second-order perturbative interactions were detected only for [ortho-  $CB_{11}H_{11}CH_3$ ]<sup>-</sup>, and their values lay in the range 0.69–2.08 kcal/mol. Thus, one can conclude that for  $BH_{3-n}(CH_3)_n$  (n = 1–3), the molecular species effect of back bonding is much more pronounced compared to in cluster species.



**Figure 5.** Values of B–C molecular orbital energies in closo-borate anions of the general form  $[B_nH_{n-1}CH_3]^{2-}$  (n = 6, 10, 12), monocarboranes  $[CB_nH_nCH_3]^{-}$  (n = 5, 9, 11) and  $BH_{3-n}(CH_3)_n$  (n = 1–3). For monocarboranes, only *exo*-polyhedral B–C bonds were considered.

The main electron density descriptors of B–C interactions were investigated using the QTAIM approach, which can provide information on many descriptors of electron density. This information includes electron density at the bond critical point (bcp), energy parameters such as the values of kinetic, potential and total energy at the bcp and the delocalisation index (Table S3). The Laplacian of electron density also provides useful information on the nature of atomic interactions (closed-shell or shared interactions). The current research focused on electron density, total energy and delocalisation indices. These descriptors have a clear physical meaning and a good correlation with other main bond descriptors, such as bond length and bond order. First, the main trends of electron density peculiarities were observed. As can be seen in Figure 6,  $BH_{3-n}(CH_3)_n$  (n = 1–3) had larger values of electron density at critical points corresponding to B-C bonds than cluster species; these were in the interval 0.180–0.186 a.u. As with bond order and orbital energy, for the carborane system with the ortho- $CH_3$  group, the values of electron density at the bcp for B–C interactions were higher than for other isomers. Carborane anions had a greater electron density at the bcp for B-C interactions than closo-borate systems. For cluster anions (closo-borate and carboranes), the main trend was for the values of electron density at the critical points corresponding to the B–C bonds to increase with increasing cluster size. The electron density at appropriate bcps had a linear negative correlation with total energy values at the bcp. Thus,  $BH_{3-n}(CH_3)_n$  (n = 1–3) also had large values of total energy at the corresponding critical points for B–C bonds (Figure 6). It is worth noting that potential energy values correlated well with other descriptors of chemical bonding and can be used as an indicator of bond strength. The values of delocalisation indices were less reliable compared to other QTAIM descriptors but still had a good level of correlation with the main descriptors of *exo*-polyhedral B–C bonds. In the case of  $BH_{3-n}(CH_3)_n$  (n = 1–3), values of delocalisation indices at corresponding critical points for B-C bonds were less than for  $[B_nH_{n-1}CH_3]^{2-}$  (n = 6, 10, 12).



**Figure 6.** Values of electron density at bond critical point (bcp) p(r) and values of total energy at bond critical point (bcp)  $H_b$  in closo-borate anions of the general form  $[B_nH_{n-1}CH_3]^{2-}$  (n = 6, 10, 12), monocarboranes  $[CB_nH_nCH_3]^-$  (n = 5, 9, 11) and  $BH_{3-n}(CH_3)_n$  (n = 1–3). For monocarboranes, only *exo*-polyhedral B–C bonds were considered.

The electron localisation function (ELF) was also used to compare the main parameters of the B–C bonds in the methylated derivatives of the closo-borate anions of the general

form  $[B_nH_{n-1}CH_3]^{2-}$  (n = 6, 10, 12). The main trend was analogous to the other bond descriptors described. It was found that the electron density values in the disynaptic pools corresponding to the B–C bonds were greater for  $BH_{3-n}(CH_3)_n$  than for the other structures considered, lying within the interval 2.03–2.04 a.u. The values of the electron occupancies in the disynaptic basins corresponding to the *exo*-polyhedral B–C bonds were in the region of 1.94–2.01 e.

It is interesting to analyse how B–C bond strength is related to atomic charges. Three different approaches (Hirshfeld, QTAIM, NBO) were applied to estimate atomic charges (Table S6). Previously, it was shown that these approaches differed from one another, except that they had the same trends in the case of closo-borate anions [51]. With the QTAIM approach, boron atoms had more positive values of charge, and hydrogen atoms had higher negative values than those obtained using the NBO and Hirshfeld approaches. General trends were the same as with unsubstituted closo-borate. As in the case of  $[B_nH_{n-1}F]^{2-}$ , the presence of the *exo*-polyhedral group influenced the charges of substituted atoms only. Based on the data obtained, it can be concluded that B–C bond strength correlates well with the value of the mean charges in the cluster. The more positive this value is, the stronger the B–C bond.

#### 3. Materials and Methods

The DFT calculations were carried out using the ORCA 4.2.1 program package [66]. Geometries of all model structures were fully optimised at the  $\omega$ B97X-D3/6-31++G(d,p) level of theory [67,68]. These range-separated DFT functional and basis sets provided accurate results for QTAIM analysis, charge density distribution and conceptual DFT descriptors [21,22]. The authors had already successfully applied this level of theory in similar studies of different boron clusters' chemical systems [23–26]. Tight criteria of SCF convergence (Tight SCF) were employed for the calculations. All of the derivatives considered had closed electron shells, and the spin-restricted approximation was applied. During the geometry optimisation procedure, symmetry operations were not applied for the structures considered. The Hessian matrices were calculated numerically for all model structures to prove the location of correct minima on potential energy surfaces (no imaginary frequencies were found, in all cases). The natural bond orbital (NBO) method was employed using the NBO7 program package [69]. Topological analysis of the electron density distribution, using the quantum theory of "Atoms in Molecules" (QTAIM) formalism developed by Bader [20], was carried out using the Multiwfn program (version 3.7) [70]. The Cartesian atomic coordinates for all optimised equilibrium model structures are presented in the Supporting Information (Table S7). The visualisation of optimised structures was carried out with the help of the ChemCraft program (version 1.7) [71].

### 4. Conclusions

The main descriptors of B–C bonds for  $[B_nH_{n-1}CH_3]^{2-}$  (n = 6, 10, 12), monocarboranes  $[CB_nH_{n-1}CH_3]^{2-}$  (n = 5, 9, 11) and  $BH_{3-n}(CH_3)_n$  (n = 1–3) were analysed. It was found that Laplacian bond order (LBO) was the best approach to describe bond orders in model species. The molecular orbital energy of the B–C bonds was a reliable descriptor of bond strength. In the case of the QTAIM approach, the following descriptors had the closest correlation with the structure of the model systems: the values of electron density and the values of total energy at the corresponding critical points. These parameters correlated well with the other bond descriptors. The difference in the nature of the chemical bonds in  $[B_nH_{n-1}CH_3]^{2-}$  and  $BH_{3-n}(CH_3)_n$  (n = 1–3) was indicated by data obtained using the ELF approach. Based on the data obtained, it can be concluded that the orbital interaction for the B–C bonds increased with increasing cluster size. For  $BH_{3-n}(CH_3)_n$  (n = 1–3), the orbital interactions were stronger than for boron cluster species. For mono-carborane systems, orbital interactions were stronger than for cluster systems, the effect of back bonding,

in which the carbon atom donates electron density to boron atoms, is significantly weaker compared to in the case with  $BH_{3-n}(CH_3)_n$  (n = 1–3) systems.

**Supplementary Materials:** The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/inorganics10110186/s1. Table S1:  $\Delta$ H—relative enthalpy energies of carborane isomers, kJ/mol,  $\Delta$ G—relative Gibbs energy of carborane isomers, kJ/mol. Table S2: B–C bond lengths and bond order descriptors. Table S3: Main topological parameters of electron density for B–C interactions. Table S4: Main parameters of molecular orbitals for B–C interactions obtained with the help of NBO formalism. Table S5: Second-order perturbation theory analysis of Fock matrix in NBO basis of *exo*-polyhedral B–C back-bonding interactions. Table S6: NBO, QTAIM and Hirshfeld atomic charges of derivatives of *closo*-borate anions [B<sub>n</sub>H<sub>n-1</sub>CH<sub>3</sub>]<sup>2–</sup> (n = 6, 10, 12), monocarboranes [CB<sub>n</sub>H<sub>n-1</sub>CH<sub>3</sub>]<sup>–</sup> (n = 5, 9, 11) and BH<sub>3–n</sub>(CH<sub>3</sub>)<sub>n</sub> n = 1–3. Figure S1: Correlation matrix of main B–C bond descriptors and mean boron atomic charges in closo-borate anions of the general form [B<sub>n</sub>H<sub>n-1</sub>CH<sub>3</sub>]<sup>2–</sup> (n = 6, 10, 12) and monocarboranes [CB<sub>n</sub>H<sub>n-1</sub>CH<sub>3</sub>]<sup>–</sup> (n = 5, 9, 11). Table S7: Cartesian atomic coordinates of the calculated optimised equilibrium model structures. All coordinates are given in Angstrom units.

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