**Theoretical study of *closo*-borate derivatives of general type [BnHn-1COR]2– (n=6,10,12; R= H, CH3, NH2, OH, OCH3) – borylated analogue of organic carbonyl compounds.**

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This study is focused on the structure, bonding, and reactivity analysis of the derivatives of *closo*-borate anions [BnHn-1COR]2– (n=6,10,12; R= H, CH3, NH2, OH, OCH3). The phenomena of B–C bonding interactions in the [BnHn-1COR]2– (n=6,10,12; R= H, CH3, NH2, OH, OCH3) have been theoretically studied by using the Quantum Theory of Atoms in Molecules. Several local and integral topological properties of the electron density involved in these interactions have been computed. Also, different chemical reactivity descriptors have been calculated via conceptual density functional theory.

**Keywords:** *DFT, closo-borate anions, reactivity descriptors, QTAIM analysis, carbonyl derivatives*

**Introduction**

Theoretical calculations devoted to bonding nature between atoms and chemical reactivity of molecules are very useful and powerful tools in modern chemistry [1–3]. These investigations allow to understand the substance structure and to design compounds with given properties. Quantum Theory of Atoms in Molecules (QTAIM) and electron localization function (ELF) analyses provide information about electron density distribution straightforwardly and clearly [4,5]. It is noteworthy that QTAIM analysis is useful in investigations of non-covalent interactions [3]. Theory of Conceptual DFT makes possible estimating chemical reactivity of compound, using only the value of HOMO and LUMO energy [6,7]. Thus, the usage of QTAIM-formalism and Conceptual DFT allows understanding the features of chemical structure and reactivity of chemical compounds in a very fascinated way [8–10].

In this work, we have focused on the application of QTAIM and Conceptual DFT Analysis to derivatives of *closo*-borate anions. There are a lot of theoretical [11,12] and experimental [13,14] investigations devoted to the chemistry of boron hydride clusters (for the comprehensive review of this topic, see[15–17]). This interest is connected to physical, chemical, and biological properties, such as high thermodynamic stability [18], magnetic properties [19,20], and low toxicity [21,22]. Previously, several boron clusters have been investigated using QTAIM analysis [23,24]. The phenomena of B-B and B-H interactions have been explored [25–27]. Also, coordination between the Cu atom and *closo*-borate anion has been investigated [11]. Conceptual DFT analysis has been used to estimate chemical reactivity of *closo*-borate anions [BnHn]2– n=10,12 [28,29].

Derivatives of boron cluster with B–C bond are interesting and important, due to their possibility of wide functionalization. For example, the main feature of [BnHn-1CO]- (n = 6, 10, 12) is easy and convenient addition reaction to the CO group [30–32]. Previously, we investigated the structure, bonding, and reactivity analysis of the mono-carbonyl derivatives of *closo*-borate anions [BnHn-1CO]– (n = 6, 10, 12) [33]. There are only several works [34,35], devoted to ELF-analysis of B-C bond in organoelement boron-contained compounds. Thus, the investigation of the nature of the B-C bond in *closo*-borate anions is an actual issue of the boron cluster chemistry.

In this work, we have explored the phenomena of B–C bonds in *closo*-borate derivatives of general type [BnHn-1COR]2– (n=6,10,12; R= H, CH3, NH2, OH, OCH3). Investigation of parametres of B–C bond can give information about stability of this bond. In this work, several local and integral topological properties of the electron density involved in these interactions have been computed. We have elaborated bond lengths, bond orders, and main topological parameters of electron density of B-C interactions. Also we have estimated analogue parametres for compounds of general type N(CH3)3BH2COR (R= H, CH3, NH2, OH, OCH3).

Theoretical analysis of chemical reactivity of closo-borate anion derivatives allowes to find the most perspective anion for selective functionalization. Using Conceptual DFT Theory it is easy to evaluate the most electrophilic molecule. The HOMO and LUMO energies, electronic chemical potential μ, chemical hardness η and softness S, and electrophilicity ω values have been explored.

**Details of calculation**

The full geometry optimization of all structures has been carried out at the ωB97X-D3/6-31++G(d,p) level of theory [36,37] with the help of the ORCA 4.1.0 program package [38]. The spin restricted approximation for the structures with closed electron shells Symmetry operations were not applied during the geometry optimization procedures for all structures. The Hessian matrices were calculated numerically for all optimized structures in order to prove the location of correct minima on the potential energy surfaces (no imaginary frequencies). The natural bond orbital (NBO) method has been utilized by using NBO7 [39]. The topological analysis of the electron density distribution with the help of the Quantum Theory of Atoms in Molecules (QTAIM) formalism developed by Bader [40] has been performed by using the Multiwfn program (version 3.6) [41]. The electronic chemical potential μ, chemical hardness η, and softness *S*, global electrophilicity ω have been calculated using the Eqs. 1-4:

(1)

(2)

(3)

(4)

Results and discussion

*B–C Bonds Geometry Parameters.* Firstly,we have considered main geometry parameters of [BnHn-1COR]2– (n=6,10,12; R= H, CH3, NH2, OH, OCH3) interactions (optimized structures of [BnHn-1COR]2– are shown in Figure 1).

The lengths of B–C interaction are shown in Table 1. For all boron clusters, the lengths of the B-C bond are similar and lie in interval 1.58-1.63 Å. The shortest B–C contacts are corresponded to [BnHn-1COH]2– for all types of *closo*-borate clusters. We compared lengths of B–C bonds in [BnHn-1COR]2– with [BnHn-1CO]–. As seen in Table 1, lengths of B–C bonds in [BnHn-1CO]– (n = 6, 10, 12) are shorter than in [BnHn-1COR]2– (n = 6, 10, 12).

*B–C Bonds Wiberg index.* The values of bond orders increase in the row:[BnHn-1CONH2]2–< [BnHn-1COOCH3]2–≈ [BnHn-1COOH]2–≈ [BnHn-1COCH3]2–< [BnHn-1COH]2– for all types of *closo*-borate clusters. Derivatives of general type [B6H5COR]2– have the maximum value of the Wiberg index. As seen in Table 1, bond orders in [BnHn-1CO]– (n = 6, 10, 12) and N(CH3)3BH2COR are greater than in [BnHn-1COR]2– (R= H, CH3, NH2, OH, OCH3).

*B–C Bonds Topological Parameters.*

The main topological parameters of B–C interaction are shown in Table 1. We have found out several general trends, which are the same for all types of *closo*-borate clusters. Derivatives of general type [2-B10H9COR]2– (R= H, CH3, NH2, OH, OCH3) have the maximum values of electron density *ρ(r)* (0.161–0.169 Å−3).The values of *ρ(r)* for all types of clusters increase in the row: [BnHn-1COOCH3]2–< [BnHn-1COOH]2–< [BnHn-1CONH2]2–< [BnHn-1COCH3]2–< [BnHn-1COH]2–. Anions [BnHn-1COH]2– have the maximum values of the delocalization index (0.165–0.169 Å−3). Anions [BnHn-1COOCH3]2– have the maximum values of ∇2*ρ(r)* (0.062–0.178 Å−3), and [BnHn-1COCH3]2–have the minimum values (0.027–0.138 Å−3). Anions [BnHn-1COH]2– have the most negative value of total energy (–0.145– –0.158 Å−3). Thus, the values of the main topological parameters for B–C interaction are typical for closed-shell dative bonding interactions [42,43].

We have compared B–C topological properties with the same in [BnHn-1CO]–. The topological properties of B–C interactions in [BnHn-1CO]– (n = 6, 10, 12) are quite different than those in [BnHn-1COR]2– (R= H, CH3, NH2, OH, OCH3). The B–C interactions of [BnHn-1CO]– are characterized by higher values of electron density *ρ(r)* comparing with [B6H5COR]2– and [1-B10H9COR]2– derivatives. [BnHn-1CO]– havemore positive values of Laplacian of electron density ∇2*ρ(r)* comparing with [BnHn-1COR]2– (R= H, CH3, NH2, OH, OCH3). The values of total energy are greater in the case of [BnHn-1COR]2– (R= H, CH3, NH2, OH, OCH3). The values of the delocalization index for carbonyl derivative compound is greater than for [BnHn-1COR]2– (R= H, CH3, NH2, OH, OCH3).

We have investigated B–C topological properties in N(CH3)3BH2COR (R= H, CH3, NH2, OH, OCH3) systems. All electron density descriptors have the same trends as in [BnHn-1COR]2–. The values of *ρ(r)* increases in the row: N(CH3)3BH2COOCH3< N(CH3)3BH2COOH≈N(CH3)3BH2CONH2< N(CH3)3BH2COCH3< N(CH3)3BH2COH. The maximum positive value of Laplacian of electron density ∇2*ρ(r)* corresponds toN(CH3)3BH2COOCH3, and the minimum positive value of Laplacian of electron density ∇2*ρ(r)* corresponds toN(CH3)3BH2COCH3. N(CH3)3BH2COHhas the most negative value of total energy, and N(CH3)3BH2COOCH3has the least negative value of total energy. The values of delocalization index follow the trend: N(CH3)3BH2COOH≈ N(CH3)3BH2CONH2< N(CH3)3BH2COOCH3< N(CH3)3BH2COCH3< N(CH3)3BH2COH.

So, the values of the main topological parameters for B–C interaction are typical for closed-shell dative bonding interactions. We have found out that for lengths of B–C bonds, Wiberg index, and topological descriptors of electron density, the main trends are the same not just for closo-borate anions but also for N(CH3)3BH2COR. [BnHn-1COH]2– (n=6,10,12) are characterized by the smallest B–C bond lengths, the highest values of Wiberg index, electron density *ρ(r),* totalenergyat the bond critical point and maximum values of the delocalization index. So in the case of [BnHn-1COH]2– (n=6,10,12) the B-C bonds are the most stabilizing,being supported by the most values of electron density *ρ(r)* and total energy Hb at bonding critical point, larger delocalization indices, δ(B,C), indicating a higher degree of electron sharing between the boron atoms and the carbon atoms.

*Non-covalent Interactions.* We have explored several non-covalent interactions between hydrogen atoms of exo-polyhedral substituents and H-atoms of boron clusters in derivatives of general type [BnHn-1COR]2– (R= H, CH3, NH2, OH, OCH3) (Table 2). Molecular graphs of anions with non-covalent interactions are shown in Figure 2. There are no non-covalent interactions for derivatives of [B6H5COR]2– (R= H, CH3, NH2, OH, OCH3) anion. Anions of general types[BnHn-1COOCH3]2–, [BnHn-1COOH]2–and [BnHn-1CONH2]2– have H-H contacts. We have observed that all H-H contacts are characterized by a small value of electron density, positive values of ∇2*ρ(r),* and total energy. Values of delocalization indexes are small and lie in interval 0.030-0.050.

In the case of [1-B10H9COOH]2– and [1-B10H9CONH2]2– we have found out one non-covalent contact between hydrogen atoms of exo-polyhedral substituents and H-atoms of boron clusters, whereas, we have found out two hydrogen bonds in case of [1-B10H9COOCH3]2–. For [1-B10H9COR]2– (R=NH2, OH, OCH3) shortest H-H contacts have been observed for [1-B10H9COOH]2– (1.93 Ǻ). Thus, this anion has maximum values of electron density and delocalization index.

In the case of [2-B10H9COR]2– there are no non-covalent contacts in the case of [2-B10H9CONH2]2–. All trends of electron density descriptors are similar to [1-B10H9COR]2– (R=NH2, OH, OCH3). For [2-B10H9COOCH3]2– we have found one hydrogen bond.

[B12H11COOH]2– has the shortest H-H contact (1.86 Ǻ) and the maximum value of electron density *ρ(r)* and delocalization index among all of the anions.Anion [B12H11COOCH3]2– has two non-covalent contacts.

Also, we have found out non-covalent interactions between O-atoms and hydrogens of methyl groups in N(CH3)3BH2COR (R= H, CH3, NH2, OH, OCH3) systems. The shortest O–H contacts correspond to N(CH3)3BH2COONH2 (2.26–2.28 Ǻ). The values of *ρ(r)* increase in the row: N(CH3)3BH2COH< N(CH3)3BH2COCH3≈ N(CH3)3BH2COOH< N(CH3)3BH2COOCH3< N(CH3)3BH2COONH2. The maximum positive value of Laplacian of electron density ∇2*ρ(r)* corresponds toN(CH3)3BH2COOCH3 and N(CH3)3BH2COONH2 and the minimum positive value of Laplacian of electron density ∇2*ρ(r)* corresponds toN(CH3)3BH2COH. For all molecules, the values of total energy are the same. The values of the delocalization index follow the same trend as *ρ(r)* ones.

*Atomic charges.* We have used QTAIM and NBO approaches for estimation of atomic charges. Both approaches (AIM and NBO) have the same trend, but in case of AIM boron and carbon atoms have a more positive charges.

Firstly, we have considered atomiccharges on B atoms bonded with *exo*-polyhedral substituent. For all *closo*-borate anions, the values of NBO atomic chargesincreases in the row: [BnHn-1COOCH3]2–≈ [BnHn-1COOH]2––< [BnHn-1COH]2–< [BnHn-1CONH2]2–≈ [BnHn-1COCH3]2–.The [B6H5COR]2– have the most negative value of Bsub atomic charge.

We have considered charges of *exo*-polyhedral carbon atoms. For all types of *closo*-borate derivatives [BnHn-1COR]2–, the values of NBO atomic chargesincrease in the row: [BnHn-1COH]2–< [BnHn-1COCH3]2–< [BnHn-1CONH2]2–< [BnHn-1COOH]2–≈ [BnHn-1COOCH3]2–. Other anions have the same trend as *closo*-hexaborate anion.

*Reactivity Analysis.* The HOMO and LUMO energies, electronic chemical potential μ, chemical hardness η and softness S, and electrophilicity ω values obtained from Eqs. (1-4) for a series of derivatives of *closo*-borate anions [BnHn-1COR]2– (n = 6, 10, 12; R= H, CH3, NH2, OH, OCH3) are shown in Table 3.

All anions [BnHn-1COR]2– (n=6,10,12; R= H, CH3, NH2, OH, OCH3) have the same trends of reactivity descriptors. All anions [BnHn-1COR]2– (R= H, CH3, NH2, OH, OCH3) have significant HOMO-LUMO gaps (6.59–8.60 eV). The values of chemical potential μ for [BnHn-1COR]2– (n=6,10,12; R= H, CH3, NH2, OH, OCH3) increase in the row: [BnHn-1COOCH3]2–<[ BnHn-1COCH3]2–<[ BnHn-1CONH2]2–< [BnHn-1COOH]2< [BnHn-1COH]2–. Anion [BnHn-1COOH]2– has the maximum value of chemical hardness, and [BnHn-1COOCH3]2– has the minimum one. The values of electrophilicity index ω increase in the row: [BnHn-1COOCH3]2–<[ BnHn-1COOH]2–<[ BnHn-1COCH3]2–< [BnHn-1CONH2]2–< [BnHn-1COH]2–. Derivatives of general type [B6H5COR]2– are the strongest electrophiles, and [B12H11COR]2– are the weakest electrophiles.

Based on the classification proposed by Domingo et al. [7,44] (electrophiles: ω > 1.50 eV strong, 1.50 > ω > 0.80 eV moderate, ω < 0.80 eV marginal); [BnHn-1COR]2– (n=6,10,12 ; R= H, CH3, NH2, OH, OCH3) can be attributed as a moderate and marginal electrophiles. Probably, this is because it is not completely correct to directly compare the electrophilicity indices of boron clusters derivatives and such parameters for organic compounds (for which Domingo’s classification was initially developed). It is only reasonable to compare the carbonyl derivatives of boron clusters between themselves.

We have estimated reactivity descriptors for N(CH3)3BH2COR (R= H, CH3, NH2, OH, OCH3) systems. As seen in Table 3 in case of this type of molecules the main reactivity descriptors are quite differ from analogue parametres for [BnHn-1COR]2– systems. The values of chemical potential μ are negative and N(CH3)3BH2COOHhas themost negative value. The values of electrophilicity index ω increase in the row: N(CH3)3BH2COCH3 < N(CH3)3BH2COH ≈N(CH3)3BH2CONH2< N(CH3)3BH2COOCH3 <N(CH3)3BH2COOH.

**Conclusions**

We carried out the comprehensive theoretical investigation of [BnHn-1COR]2– (n=6,10,12; R= H, CH3, NH2, OH, OCH3). The nature of B–C bonds and intermolecular non-covalent interactions in [BnHn-1COR]2– have been studied. The main reactivity descriptors of explored anions also have been studied.

The values of the main topological parameters for B–C interaction are typical for closed-shell dative bonding interactions. We have found out that for lengths of B–C bonds, Wiberg index, and topological descriptors of electron density, the main trends are the same not just for closo-borate anions but also for N(CH3)3BH2COR. [BnHn-1COH]2– (n=6,10,12) are characterized by the smallest B–C bond lengths, the highest values of Wiberg index, electron density *ρ(r),* totalenergyat the bond critical point and maximum values of the delocalization index. So in the case of [BnHn-1COH]2– (n=6,10,12) the B-C bonds are the most stabilizing,being supported by the most value of electron density at bonding critical point, larger delocalization indices, δ(B,C), indicating a higher degree of electron sharing between the boron atoms and the carbon atoms.

We have explored several non-covalent interactions between hydrogen atoms of exo-polyhedral substituents and H-atoms of boron clusters in derivatives of general type [BnHn-1COR]2–. There are no non-covalent interactions for derivatives of [B6H5COR]2– (R= H, CH3, NH2, OH, OCH3) anion. Anions of general types[BnHn-1COOCH3]2–, [BnHn-1COOH]2– (n=10,12) and [BnHn-1CONH2]2– have intermolecular H-H contacts. We have observed that all H-H contacts are characterized by the value of electron density between 0.009 and 0.018 e Å−3, positive values of ∇2*ρ(r),* and total energy. Values of delocalization indexes lie in interval 0.030-0.050.

We have estimated reactivity descriptors of [BnHn-1COR]2– (n=6,10,12; R= H, CH3, NH2, OH, OCH3) using Conceptual DFT theory. Using the information from these calculation allowes to establish the most convenient anions for further functionalization. The more electrophilic nature closo-borate anion has, the more softly reaction of nucleophilic addition goes. The values of electrophilicity index ω increase in the row: [BnHn-1COOCH3]2–<[BnHn-1COOH]2–<[BnHn-1COCH3]2–< [BnHn-1CONH2]2–< [BnHn-1COH]2–. Derivatives of general type [B6H5COR]2– are the strongest electrophiles, and [B12H11COR]2– are the weakest electrophiles. So, based on Conceptual DFT theory calculation we have explored that derivatives of closo-hexaborate derivatives of general form are the most convenient platform for reaction of nucleophilic addition.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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**Reference**

[1] L. Zhao, S. Pan, N. Holzmann, P. Schwerdtfeger, G. Frenking, Chemical Bonding and Bonding Models of Main-Group Compounds, Chem. Rev. 119 (2019) 8781–8845. doi:10.1021/acs.chemrev.8b00722.

[2] F. Cortés-Guzmán, R.F.W. Bader, Complementarity of QTAIM and MO theory in the study of bonding in donor-acceptor complexes, Coord. Chem. Rev. 249 (2005) 633–662. doi:10.1016/j.ccr.2004.08.022.

[3] D.S. Allgäuer, H. Jangra, H. Asahara, Z. Li, Q. Chen, H. Zipse, A.R. Ofial, H. Mayr, Quantification and Theoretical Analysis of the Electrophilicities of Michael Acceptors, J. Am. Chem. Soc. 139 (2017) 13318–13329. doi:10.1021/jacs.7b05106.

[4] I. Vidal, S. Melchor, J.A. Dobado, On the nature of metal - Carbon bonding: AIM and ELF analyses of MCH n (n = 1-3) compounds containing early transition metals, J. Phys. Chem. A. 109 (2005) 7500–7508. doi:10.1021/jp050146q.

[5] A. Savin, R. Nesper, S. Wengert, T.F. Fässler, ELF: The electron localization function, Angew. Chemie (International Ed. English). 36 (1997) 1808–1832. doi:10.1002/anie.199718081.

[6] P. Geerlings, E. Chamorro, P.K. Chattaraj, F. De Proft, J.L. Gázquez, S. Liu, C. Morell, A. Toro-Labbé, A. Vela, P. Ayers, Conceptual density functional theory: status, prospects, issues, Theor. Chem. Acc. 139 (2020) 1–18. doi:10.1007/s00214-020-2546-7.

[7] L.R. Domingo, M.J. Aurell, P. Pérez, R. Contreras, Quantitative characterization of the global electrophilicity power of common diene/dienophile pairs in Diels-Alder reactions, Tetrahedron. 58 (2002) 4417–4423. doi:10.1016/S0040-4020(02)00410-6.

[8] J. Oller, P. Pérez, P.W. Ayers, E. Vöhringer-Martinez, Global and local reactivity descriptors based on quadratic and linear energy models for α,β-unsaturated organic compounds, Int. J. Quantum Chem. 118 (2018) 1–13. doi:10.1002/qua.25706.

[9] A.S. Novikov, 1,3-Dipolar cycloaddition of nitrones to transition metal-bound isocyanides: DFT and HSAB principle theoretical model together with analysis of vibrational spectra, J. Organomet. Chem. 797 (2015) 8–12. doi:10.1016/j.jorganchem.2015.07.024.

[10] R. Aliveisi, A. Taherpour, I. Yavari, A DFT Study of Electronic Structures and Relative Stabilities of Isomeric n,m-Diazaphenanthrenes, Polycycl. Aromat. Compd. 39 (2019) 462–469. doi:10.1080/10406638.2017.1343195.

[11] A. V Vologzhanina, A.A. Korlyukov, V. V Avdeeva, I.N. Polyakova, E.A. Malinina, N.T. Kuznetsov, Theoretical QTAIM , ELI-D , and Hirshfeld Surface Analysis of the Cu−(H)B Interaction in [Cu2(bipy )2B10H10], J. Phys. Chem. A. 2 (2013) 13138.

[12] V.K. Kochnev, N.T. Kuznetsov, Theoretical study of protonation of the B10H10 2- anion and subsequent hydrogen removal due to substitution reaction in acidic medium, Comput. Theor. Chem. 1075 (2016) 77–81. doi:10.1016/j.comptc.2015.11.014.

[13] Y. Zhang, Y. Sun, F. Lin, J. Liu, S. Duttwyler, Rhodium(III)-Catalyzed Alkenylation???Annulation of closo-Dodecaborate Anions through Double B???H Activation at Room Temperature, Angew. Chemie - Int. Ed. 55 (2016) 15609–15614. doi:10.1002/anie.201607867.

[14] P. Kaszyński, B. Ringstrand, Functionalization of closo-borates via iodonium zwitterions, Angew. Chemie - Int. Ed. 54 (2015) 6576–6581. doi:10.1002/anie.201411858.

[15] D. Olid, R. Núñez, C. Viñas, F. Teixidor, Methods to produce B-C, B-P, B-N and B-S bonds in boron clusters., Chem. Soc. Rev. 42 (2013) 3318–36. doi:10.1039/c2cs35441a.

[16] A.A. Semioshkin, I.B. Sivaev, V.I. Bregadze, Cyclic oxonium derivatives of polyhedral boron hydrides and their synthetic applications, Dalt. Trans. 11 (2008) 977–992. doi:10.1039/b715363e.

[17] K.Y. Zhizhin, A.P. Zhdanov, N.T. Kuznetsov, Derivatives of closo-decaborate anion [B10H10]2− with exo-polyhedral substituents, Russ. J. Inorg. Chem. 55 (2010) 2089–2127. doi:10.1134/S0036023610140019.

[18] L. Duchêne, R.S. Kühnel, D. Rentsch, A. Remhof, H. Hagemann, C. Battaglia, A highly stable sodium solid-state electrolyte based on a dodeca/deca-borate equimolar mixture, Chem. Commun. 53 (2017) 4195–4198. doi:10.1039/c7cc00794a.

[19] N.T. Kuznetsov, L.G. Lavrenova, A.S. Bogomyakov, K.Y. Zhizhin, O.G. Shakirova, Synthesis and magnetic properties of iron(II) closo-borate complexes with tris(3,5-dimethylpyrazol-1-yl)methane, Russ. J. Inorg. Chem. 60 (2015) 786–789. doi:10.1134/s003602361507013x.

[20] O.G. Shakirova, S. V. Trubina, V.A. Daletskii, N.T. Kuzhetsov, K.Y. Zhizhin, L.G. Lavrenova, S.B. Erenburg, Iron(II) closo-borate complexes with 1,2,4-triazole derivatives: Spin crossover in the iron(II) closo-borate complexes with tris(pyrazol-1-yl)methane, Russ. J. Inorg. Chem. 58 (2013) 650–656. doi:10.1134/s0036023613060211.

[21] M.Y. Losytskyy, V.B. Kovalska, O.A. Varzatskii, M. V. Kuperman, S. Potocki, E. Gumienna-Kontecka, A.P. Zhdanov, S.M. Yarmoluk, Y.Z. Voloshin, K.Y. Zhizhin, N.T. Kuznetsov, A. V. Elskaya, An interaction of the functionalized closo-borates with albumins: The protein fluorescence quenching and calorimetry study, J. Lumin. 169 (2016) 51–60. doi:10.1016/j.jlumin.2015.08.042.

[22] M. Kuperman, S. Chernii, O. Varzatskii, A. Zhdanov, A. Bykov, K. Zhizhin, S. Yarmoluk, V. Kovalska, The Discovery of the Effect of closo-Borate on Amyloid Fibril Formation, ChemistrySelect. 2 (2017) 10965–10970. doi:10.1002/slct.201701936.

[23] E.G. Kononova, L.A. Leites, S.S. Bukalov, I. V. Pisareva, I.T. Chizhevsky, J.D. Kennedy, J. Bould, Vibrational spectrum and electronic structure of the [B11H 11]2- dianion, Eur. J. Inorg. Chem. (2007) 4911–4918. doi:10.1002/ejic.200700461.

[24] E.G. Kononova, L.A. Leites, S.S. Bukalov, I. V. Pisareva, I.T. Chizhevsky, Experimental and theoretical study of the vibrational spectrum, structure and electron density distribution of neutral 11-vertex dicarbaborane 2,3-C2B9H11, J. Mol. Struct. 794 (2006) 148–153. doi:10.1016/j.molstruc.2006.01.051.

[25] E.G. Kononova, L.A. Leites, S.S. Bukalov, A. V. Zabula, I. V. Pisareva, V.E. Konoplev, I.T. Chizhevsky, Experimental and theoretical study of the vibrational spectrum, structure and electron density distribution of the [2-CB10H11] - anion, Chem. Phys. Lett. 390 (2004) 279–284. doi:10.1016/j.cplett.2004.04.025.

[26] E.G. Kononova, Z.S. Klemenkova, The electronic structure of nido-B10H14 and [6-Ph-nido-6-CB9H11]- in terms of Bader’s theory (AIM), J. Mol. Struct. 1036 (2013) 311–317. doi:10.1016/j.molstruc.2012.11.053.

[27] D. Sethio, L.M.L. Daku, H. Hagemann, E. Kraka, Quantitative Assessment of B−B−B, B−Hb−B, and B−Ht Bonds: From BH3 to B12H122−, ChemPhysChem. 20 (2019) 1967–1977. doi:10.1002/cphc.201900364.

[28] V.K. Kochnev, V.V. Avdeeva, E.A. Malinina, N.T. Kuznetsov, Theoretical study of H2 Elimination from [BnHn+1] monoanions (n = 6-9, 11), Russ. J. Inorg. Chem. 59 (2014) 1268–1275. doi:10.1134/S0036023614110102.

[29] V.K. Kochnev, V.V. Avdeeva, E.A. Malinina, N.T. Kuznetsov, Theoretical study of molecular hydrogen elimination from the undecahydrodecaborate monoanion [B10H11]-. Exopolyhedral substitution intermediates: [B10H9] - monoanion and neutral [B10H10] Cluster, Russ. J. Inorg. Chem. 59 (2014) 706–712. doi:10.1134/S0036023614070079.

[30] I.N. Klyukin, N.A. Selivanov, A.Y. Bykov, A.P. Zhdanov, K.Y. Zhizhin, N.T. Kuznetsov, Synthesis and Physicochemical Properties of C-Borylated Amides Based on the closo-Decaborate Anion, Russ. J. Inorg. Chem. 64 (2019) 1405–1409. doi:10.1134/S0036023619110081.

[31] D.S. Wilbur, M. Chyan, H. Nakamae, Y. Chen, D.K. Hamlin, E.B. Santos, B.T. Kornblit, B.M. Sandmaier, D. Scott Wilbur, \* , † Ming-Kuan Chyan, † Hirohisa Nakamae, § Yun Chen, § Donald K. Hamlin, † Erlinda B. Santos, § Brian T. Kornblit, § and Brenda M. Sandmaier ‡ , §, Bioconjug. Chem. 23 (2012) 409–420.

[32] D.S. Wilbur, M.K. Chyan, D.K. Hamlin, M.A. Perry, Preparation and in vivo evaluation of radioiodinated closo-decaborate(2-) derivatives to identify structural components that provide low retention in tissues, Nucl. Med. Biol. 37 (2010) 167–178. doi:10.1016/j.nucmedbio.2009.10.004.

[33] I.N. Klyukin, A.S. Novikov, A.P. Zhdanov, K.Y. Zhizhin, N.T. Kuznetsov, Theoretical study of monocarbonyl derivatives of closo-borate anions [BnHn–1CO]– (n = 6, 10, 12): bonding and reactivity analysis, Mendeleev Commun. 30 (2020) 88–90. doi:10.1016/j.mencom.2020.01.029.

[34] G. Mierzwa, A.J. Gordon, S. Berski, Topological analysis of electron localisation function: Unlocking the nature of B–C chemical bond. Possible existence of multiple bonds B[dbnd]C and B[tbnd]C, Polyhedron. 170 (2019) 180–187. doi:10.1016/j.poly.2019.05.035.

[35] M.E. Alikhani, On the chemical bonding features in boron containing compounds: A combined QTAIM/ELF topological analysis, Phys. Chem. Chem. Phys. 15 (2013) 12602–12609. doi:10.1039/c3cp50396h.

[36] J. Da Chai, M. Head-Gordon, Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections, Phys. Chem. Chem. Phys. 10 (2008) 6615–6620. doi:10.1039/b810189b.

[37] W.J. Hehre, K. Ditchfield, J.A. Pople, Self-consistent molecular orbital methods. XII. Further extensions of gaussian-type basis sets for use in molecular orbital studies of organic molecules, J. Chem. Phys. 56 (1972) 2257–2261. doi:10.1063/1.1677527.

[38] F. Neese, The ORCA program system, WIREs Comput. Mol . Sci. 2 (2012) 73–78. doi:10.1002/wcms.81.

[39] A.E.R. NBO 7.0. E. D. Glendening, J. K. Badenhoop, P.K. J. E. Carpenter, J. A. Bohmann, C. M. Morales, T.C.I. C. R. Landis, and F. Weinhold, W. (2018) University of Wisconsin, Madison, No Title, (n.d.).

[40] R.F.W. Bader, Atoms in Molecules: A Quantum Theory, Oxford University Press, Oxford, 1990.

[41] T. Lu, F. Chen, Multiwfn : A Multifunctional Wavefunction Analyzer, J. Comp. Chem. 33 (2011) 580–592. doi:10.1002/jcc.22885.

[42] R. Bader, D. Legare, Properties of atoms in molecules: structures and reactivities of boranes and carboranes, Can. J. Chem. 70 (1992) 657–677.

[43] S.J. Grabowski, What Is the Covalency of Hydrogen Bonding?, Chem. Rev. 111 (2011) 2597–2625. doi:10.1021/cr800346f.

[44] L.R. Domingo, M. Ríos-Gutiérrez, P. Pérez, Applications of the conceptual density functional theory indices to organic chemistry reactivity, Molecules. 21 (2016) 748–770. doi:10.3390/molecules21060748.

**Table 1.** B–Cbondlength**s,** Wiberg Index,Maintopological parameters of electron density for B–C interactions. ρ(r) – Electron density at the bcp. ∇2ρ(r) - Laplacian of electron density at the bcp. Hb – total energy at the bcp. δ(B–C) – delocalization index. ɛb – ellipticity at the bcp.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Anion | B–C length,  Å | Wiberg Index | *ρ(r)*  (e Å−3) | ∇2*ρ(r)*  (e Å−5) | Hb  (h e−1) | δ(B–C) | εb |
|  | | | | | | |  |
| [B6H5COOH]2– | 1.59 | 0.94 | 0.158 | 0.164 | -0.139 | 0.629 | 0,088 |
| [B6H5COOСH3]2– | 1.60 | 0.94 | 0.155 | 0.178 | -0.134 | 0.631 | 0,074 |
| [B6H5CONH2]2– | 1.60 | 0.92 | 0.158 | 0.143 | -0.140 | 0.629 | 0,077 |
| [B6H5COH]2– | 1.58 | 0.99 | 0.166 | 0.152 | -0.148 | 0.679 | 0,095 |
| [B6H5COCH3]2– | 1.59 | 0.94 | 0.163 | 0.138 | -0.145 | 0.658 | 0,086 |
| [B6H5CO]– | 1.45 | 1.22 | 0.171 | 0.669 | -0.127 | 0.923 | 0,000 |
|  | | | | | | |  |
| [1-B10H9COOH]2– | 0,072 | 0,072 | 0,072 | 0,072 | 0,072 | 0,072 | 0,072 |
| [1-B10H9COOCH3]2– | 0,062 | 0,062 | 0,062 | 0,062 | 0,062 | 0,062 | 0,062 |
| [1-B10H9CONH2]2– | 0,067 | 0,067 | 0,067 | 0,067 | 0,067 | 0,067 | 0,067 |
| [1-B10H9COH]2– | 0,084 | 0,084 | 0,084 | 0,084 | 0,084 | 0,084 | 0,084 |
| [1-B10H9COCH3]2– | 0,080 | 0,080 | 0,080 | 0,080 | 0,080 | 0,080 | 0,080 |
| [1-B10H9CO]– | 0,000 | 0,000 | 0,000 | 0,000 | 0,000 | 0,000 | 0,000 |
|  | | | | | | |  |
| [2-B10H9COOH]2– | 0,206 | 0,206 | 0,206 | 0,206 | 0,206 | 0,206 | 0,206 |
| [2-B10H9COOCH3]2– | 0,222 | 0,222 | 0,222 | 0,222 | 0,222 | 0,222 | 0,222 |
| [2-B10H9CONH2]2– | 0,218 | 0,218 | 0,218 | 0,218 | 0,218 | 0,218 | 0,218 |
| [2-B10H9COH]2– | 0,222 | 0,222 | 0,222 | 0,222 | 0,222 | 0,222 | 0,222 |
| [2-B10H9COCH3]2– | 0,219 | 0,219 | 0,219 | 0,219 | 0,219 | 0,219 | 0,219 |
| [2-B10H9CO]– | 0,203 | 0,203 | 0,203 | 0,203 | 0,203 | 0,203 | 0,203 |
|  | | | | | | |  |
| [B12H11COOH]2– | 0,058 | 0,058 | 0,058 | 0,058 | 0,058 | 0,058 | 0,058 |
| [B12H11COOCH3]2– | 0,049 | 0,049 | 0,049 | 0,049 | 0,049 | 0,049 | 0,049 |
| [B12H11CONH2]2– | 0,053 | 0,053 | 0,053 | 0,053 | 0,053 | 0,053 | 0,053 |
| [B12H11COH]2– | 0,060 | 0,060 | 0,060 | 0,060 | 0,060 | 0,060 | 0,060 |
| [B12H11COCH3]2– | 0,058 | 0,058 | 0,058 | 0,058 | 0,058 | 0,058 | 0,058 |
| [B12H11CO]2– | 0,001 | 0,001 | 0,001 | 0,001 | 0,001 | 0,001 | 0,001 |
|  | | | | | | |  |
| NMe3BH2COOH | 0,231 | 0,231 | 0,231 | 0,231 | 0,231 | 0,231 | 0,231 |
| NMe3BH2COOCH3 | 0,229 | 0,229 | 0,229 | 0,229 | 0,229 | 0,229 | 0,229 |
| NMe3BH2CONH2 | 0,224 | 0,224 | 0,224 | 0,224 | 0,224 | 0,224 | 0,224 |
| NMe3BH2COH | 0,229 | 0,229 | 0,229 | 0,229 | 0,229 | 0,229 | 0,229 |
| NMe3BH2COCH3 | 0,230 | 0,230 | 0,230 | 0,230 | 0,230 | 0,230 | 0,230 |

**Table 2.** Maintopological parameters of electron density for H–H interactions, ρ(r) – Electron density at the bcp. ∇2ρ(r) - Laplacian of electron density at the bcp, Hb – total energy at the bcp, ɛ – ellipticity at the bcp. δ(A-B) – delocalization index.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Anion | H–H length.  Å | *ρ(r)*  (e Å−3) | ∇2*ρ(r)*  (e Å−5) | Hb  (h e−1) | δ(B–C) | εb |
| [1-B10H9COOH]2– | 1.93 | 0.017 | 0.049 | 0.001 | 0.044 | 0.044 |
| [1-B10H9COOCH3]2– | 2.23 | 0.010 | 0.033 | 0.002 | 0.038 | 0.038 |
|  | 2.21 | 0.010 | 0.034 | 0.002 | 0.039 | 0.039 |
| [1-B10H9CONH2]2– | 2.13 | 0.011 | 0.039 | 0.002 | 0.034 | 0.034 |
|  |  |  |  |  |  |  |
| [2-B10H9COOH]2– | 1.95 | 0.016 | 0.048 | 0.001 | 0.039 | 0.039 |
| [2-B10H9COCH3]2– | 2.31 | 0.009 | 0.030 | 0.002 | 0.039 | 0.039 |
|  |  |  |  |  |  |  |
| [B12H11COOH]2– | 1.86 | 0.018 | 0.051 | 0.001 | 0.050 | 0.050 |
| [B12H11COOCH3]2– | 2.28 | 0.009 | 0.034 | 0.002 | 0.031 | 0.031 |
|  | 2.07 | 0.013 | 0.041 | 0.002 | 0.046 | 0.046 |
| [B12H11CONH2]2– | 2.03 | 0.013 | 0.043 | 0.002 | 0.040 | 0.040 |
|  |  |  |  |  |  |  |
| NMe3BH2COOH | 2.31 | 0.015 | 0.048 | 0.001 | 0.051 | 0.051 |
|  | 2.31 | 0.015 | 0.048 | 0.001 | 0.051 | 0.051 |
| NMe3BH2COOCH3 | 2.28 | 0.016 | 0.051 | 0.001 | 0.053 | 0.053 |
|  | 2.27 | 0.016 | 0.053 | 0.001 | 0.055 | 0.055 |
| NMe3BH2CONH2 | 2.28 | 0.016 | 0.051 | 0.001 | 0.055 | 0.055 |
|  | 2.26 | 0.017 | 0.053 | 0.000 | 0.058 | 0.058 |
| NMe3BH2COH | 2.34 | 0.014 | 0.046 | 0.001 | 0.048 | 0.048 |
|  | 2.34 | 0.014 | 0.046 | 0.001 | 0.049 | 0.049 |
| NMe3BH2COCH3 | 2.30 | 0.015 | 0.049 | 0.001 | 0.051 | 0.051 |
|  | 2.31 | 0.015 | 0.049 | 0.001 | 0.052 | 0.052 |

**Table 3**. HOMO and LUMO energies, electronic chemical potential μ, chemical hardness η and softness S, and electrophilicity ω.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Anion | HOMO.  eV | LUMO.  eV | Gap.  eV | chem potential. μ. eV | Electro  negativity. χ.  eV | chemical hardness. η.  eV | chemical softness. S. eV–1 | electrophilicity index. ω. eV |
| [B6H5COOH]2– | 0.27 | 6.86 | 6.59 | 3.57 | -3.57 | 6.59 | 0.15 | 0.96 |
| [B6H5COOСH3]2– | 0.37 | 5.95 | 5.58 | 3.16 | -3.16 | 5.58 | 0.18 | 0.90 |
| [B6H5CONH2]2– | 0.53 | 6.32 | 5.78 | 3.42 | -3.42 | 5.78 | 0.17 | 1.01 |
| [B6H5COH]2– | 0.55 | 6.94 | 6.38 | 3.74 | -3.74 | 6.38 | 0.16 | 1.10 |
| [B6H5COCH3]2– | 0.53 | 6.23 | 5.70 | 3.38 | -3.38 | 5.70 | 0.18 | 1.00 |
|  |  |  |  |  |  |  |  |  |
| [1-B10H9COOH]2– | -0.93 | 6.46 | 7.39 | 2.77 | -2.77 | 7.39 | 0.14 | 0.52 |
| [1-B10H9COOCH3]2– | -0.83 | 5.53 | 6.35 | 2.35 | -2.35 | 6.35 | 0.16 | 0.43 |
| [1-B10H9CONH2]2– | -0.68 | 5.91 | 6.59 | 2.61 | -2.61 | 6.59 | 0.15 | 0.52 |
| [1-B10H9COH]2– | -0.66 | 6.53 | 7.19 | 2.94 | -2.94 | 7.19 | 0.14 | 0.60 |
| [1-B10H9COCH3]2– | -0.69 | 5.80 | 6.49 | 2.56 | -2.56 | 6.49 | 0.15 | 0.50 |
|  |  |  |  |  |  |  |  |  |
| [2-B10H9COOH]2– | -0.89 | 6.46 | 7.35 | 2.78 | -2.78 | 7.35 | 0.14 | 0.53 |
| [2-B10H9COOCH3]2– | -0.78 | 5.57 | 6.35 | 2.40 | -2.40 | 6.35 | 0.16 | 0.45 |
| [2-B10H9CONH2]2– | -0.67 | 6.00 | 6.67 | 2.67 | -2.67 | 6.67 | 0.15 | 0.53 |
| [2-B10H9COH]2– | -0.68 | 6.54 | 7.22 | 2.93 | -2.93 | 7.22 | 0.14 | 0.59 |
| [2-B10H9COCH3]2– | -0.67 | 5.87 | 6.54 | 2.60 | -2.60 | 6.54 | 0.15 | 0.52 |
|  |  |  |  |  |  |  |  |  |
| [B12H11COOH]2– | -2.29 | 6.30 | 8.60 | 2.00 | -2.00 | 8.60 | 0.12 | 0.23 |
| [B12H11COOCH3]2– | -2.20 | 5.46 | 7.66 | 1.63 | -1.63 | 7.66 | 0.13 | 0.17 |
| [B12H11CONH2]2– | -1.97 | 5.82 | 7.79 | 1.93 | -1.93 | 7.79 | 0.13 | 0.24 |
| [B12H11COH]2– | -1.81 | 6.35 | 8.17 | 2.27 | -2.27 | 8.17 | 0.12 | 0.32 |
| [B12H11COCH3]2– | -1.78 | 5.70 | 7.49 | 1.96 | -1.96 | 7.49 | 0.13 | 0.26 |