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Theoretical study of monocarbonyl derivatives of *closo*-borate anions $[B_nH_{n-1}CO]^-$ (n = 6, 10, 12): bonding and reactivity analysis

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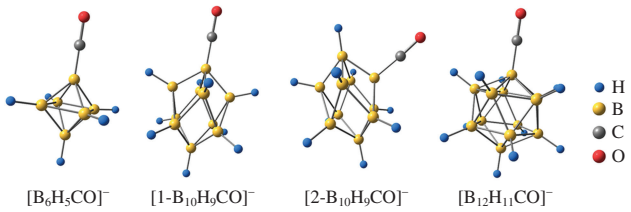
The structure, bonding, and reactivity of the monocarbonyl derivatives of *closo*-borate anions $[B_nH_{n-1}CO]^-$ (n = 6, 10, 12) have been analyzed. The B–B, B–H, B–C and C–O bonding interactions in such anions have been theoretically examined using the Quantum Theory of Atoms in Molecules (QTAIM). Several local and integral topological properties of the electron density involved in these interactions have been computed, and different chemical reactivity descriptors have been calculated *via* conceptual density functional theory (DFT).



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Nowadays, many theoretical[1,2] and experimental[3,4] investigations on chemistry of boron hydride clusters have been carried out (for comprehensive review on this topic see refs. 5–7). This interest is connected with physical, chemical and biological properties such as high thermodynamic stability,[8] magnetic properties,[9,10] and low toxicity.[11,12] Various *closo*-borate derivatives with *exo*-polyhedral B–C bonds have also been studied experimentally[13,14] and theoretically.[15,16] Carbonyl derivatives of *closo*-borate anions $[B_nH_{n-1}CO]^-$ (n = 6, 10, 12) are the most unique and interesting boron polyhedral compounds with a B–C bond. These molecules are very stable to oxidation when exposed to air even as an aqueous solution.[13] The main feature of $[B_nH_{n-1}CO]^-$ (n = 6, 10, 12) is their easy and convenient functionalization using addition reactions to the carbonyl group.

It is noteworthy that the phenomenon of *exo*-polyhedral B–C bond in various boron cluster compounds has not been studied previously. Moreover, there are only several works[17,18] related to ELF-analysis B–C bond in organoboron compounds. Thus, the investigation of B–C bond nature in *closo*-borate anions is a topical question in the boron cluster chemistry.

In this contribution, we have focused on the systematic theoretical analysis of structure, bonding and reactivity of carbonyl derivatives of *closo*-borate anions $[B_nH_{n-1}CO]^-$ (n = 6, 10, 12), which is of importance for the development of synthetic approaches towards organoboron molecules with useful properties.

Optimized equilibrium structures of monocarbonyl derivatives of *closo*-decaborate anions are shown in Figure 1. Geometry optimization of all structures has been carried out at the ωB97X-D3/6-31++G(d,p) level of theory using ORCA 4.1.0 program package.[19] The spin restricted approximation for the structures with closed electron shells and the unrestricted approach for the structures with open electron shells have been employed. More computational details and the discussion of calculated effective atomic charges are presented in Online Supplementary Materials.

First, we have considered main geometric parameters of monocarbonyl derivatives of *closo*-borate anions. The B–B bond length values of 1.70–1.90 Å, and the B–H bond length values of 1.19–1.21 Å are close to those obtained for the corresponding $[B_nH_n]^{2-}$ anions.[20,21] The B–C bond length is 1.45–1.50 Å, which is in a good agreement with previously reported theoretical and experimental results.[15] The length of B–C bond increases with the increase of boron cluster size. We have compared these values with the B–C bond in some organoboron compounds $BH_{3-n}R_n$, n = 1–3 and BH_3CO geometry calculated on the same level of theory [ωB97X-D3/6-31++G(d,p)]. The B–C bond lengths in $BH_{3-n}R_n$, n = 1–3 are 1.56–1.58 Å and are slightly longer than those in polyhedral clusters. The values of C–O bond length decrease with the increase of boron clusters size. The C–O bond length (1.13 Å) in BH_3CO is slightly smaller than those in polyhedral clusters.

The B–B, B–H, B–C and C–O bonding interactions in the monocarbonyl derivatives of *closo*-borate anions $[B_nH_{n-1}CO]^-$

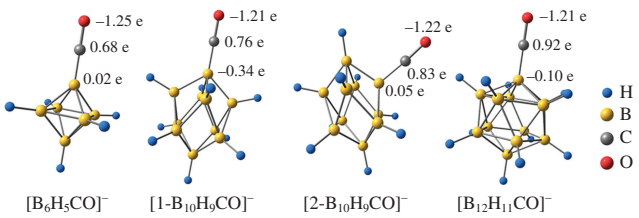

Figure 1 Optimized structures of anions $[B_nH_{n-1}CO]^-$ (n = 6, 10, 12). AIM charges on selected atoms are shown.

(n = 6, 10, 12) have been theoretically studied using the Quantum Theory of Atoms in Molecules (QTAIM), and several local and integral topological properties of the electron density involved in these interactions have been computed. For main topological parameters of electron density for B–B and B–H interactions, see Online Supplementary Materials.

These values of topological properties are close to those previously reported for the corresponding $[B_nH_n]^{2-}$ anions.[20]

The main topological parameters of B–C interaction are given in Table 1. The $\rho(r)$ values of B–C interactions decrease with the increase of boron clusters size. The $\nabla^2\rho(r)$ values follow the same trend as the $\rho(r)$ ones. The total energy values are negative, and $[B_6H_5CO]^-$ has the most negative value. The maximum delocalization index is 0.923 ($[B_6H_5CO]^-$), and the minimum value of delocalization index is 0.746 ($[B_{12}H_{11}CO]^-$). Thus, the values of main topological parameters for B–C interaction are typical of closed shell dative bonding interactions.[20,22]

It is of interest to compare B–C topological properties in other systems such as simple organoboron compounds $BH_{3-n}R_n$ (n = 1–3) and BH_3CO. The topological properties of B–C interactions in $BH_{3-n}R_n$ (n = 1–3) are quite different from those in $[B_nH_{n-1}CO]^-$ (n = 6, 10, 12). The B–C interactions of the former are characterized by greater values of electron density $\rho(r)$ and more negative values of the Laplacian of electron density $\nabla^2\rho(r)$ as compared to the latter. The values of delocalization index for simple organoboron compounds are less than those for $[B_nH_{n-1}CO]^-$ (n = 6, 10, 12).

The main topological parameters for C–O interaction are given in Table 1. All topological properties of C–O interactions have opposite trends as compared to those of B–C interactions. The maximum value of $\rho(r)$ is 0.468 e Å^{-3} ($[B_{12}H_{11}CO]^-$) and minimum value is 0.450 e Å^{-3} ($[B_6H_5CO]^-$). The total energy values are negative, $[B_6H_5CO]^-$ having the most negative one. The values of delocalization index are 1.470–1.532.

The C–O bond length (1.13 Å) in BH_3CO is slightly shorter than that in polyhedral cluster; the corresponding value of $\rho(r)$ (0.473 e Å^{-3}) is greater than that for carbonyl derivatives of boron cluster. The positive value of Laplacian of electron density $\nabla^2\rho(r)$ of C–O interaction in BH_3CO is greater than that in $[B_nH_{n-1}CO]^-$ (n = 6, 10, 12). The value of delocalization index of C–O interaction in BH_3CO is 1.560.

Table 1 Main topological parameters of electron density for B–C and C–O interactions.[a]

Model structure	Bond (A–B) length/Å	$\rho(r)$/ e Å^{-3}	$\nabla^2\rho(r)$/ e Å^{-5}	H_b/h e^{-1}	ε	δ(A–B)
		B–C interactions				
$[B_6H_5CO]^-$	1.45	0.171	0.669	–0.126	0.000	0.923
$[1\text{-}B_{10}H_9CO]^-$	1.46	0.169	0.666	–0.125	0.000	0.892
$[2\text{-}B_{10}H_9CO]^-$	1.48	0.162	0.611	–0.120	0.203	0.783
$[B_{12}H_{11}CO]^-$	1.50	0.156	0.597	–0.113	0.001	0.747
BH_3CO	1.54	0.138	0.604	–0.094	0.004	0.429
$MeBH_2$	1.56	0.186	–0.153	–0.191	0.293	0.525
Me_2BH	1.57	0.183	–0.138	–0.187	0.283	0.497
Me_3B	1.58	0.180	–0.136	–0.183	0.284	0.474
		C–O interactions				
$[B_6H_5CO]^-$	1.16	0.450	0.987	–0.746	0.000	1.470
$[1\text{-}B_{10}H_9CO]^-$	1.15	0.458	1.080	–0.762	0.000	1.509
$[2\text{-}B_{10}H_9CO]^-$	1.15	0.461	1.126	–0.765	0.001	1.510
$[B_{12}H_{11}CO]^-$	1.14	0.468	1.216	–0.778	0.000	1.533
BH_3CO	1.14	0.473	1.276	–0.787	0.000	1.560

[a] $\rho(r)$ – electron density at the bcp, $\nabla^2\rho(r)$ – Laplacian of the electron density at the bcp, H_b – total energy at the bcp, ε – ellipticity at the bcp, δ(A–B) – delocalization index.

Table 2 HOMO and LUMO energies, electronic chemical potential μ, electronegativity χ, chemical hardness η and softness S, and electrophilicity ω for $[B_nH_{n-1}CO]^-$ (n = 6, 10, 12).

Anion	HOMO/ eV	LUMO/ eV	Gap/ eV	μ/eV	χ/eV	η/eV	S/eV^{-1}	ω/eV
$[B_6H_5CO]^-$	–4.05	4.22	8.28	0.08	–0.08	8.28	0.12	0.00
$[1\text{-}B_{10}H_9CO]^-$	–5.14	3.35	8.50	–0.90	0.90	8.50	0.12	0.05
$[2\text{-}B_{10}H_9CO]^-$	–4.85	3.21	8.07	–0.82	0.82	8.07	0.12	0.04
$[B_{12}H_{11}CO]^-$	–6.13	2.98	9.13	–1.57	1.57	9.13	0.11	0.14

The HOMO and LUMO energies, electronic chemical potential μ, chemical hardness η and softness S, and electrophilicity ω values for a series of monocarbonyl derivatives of *closo*-borate anions $[B_nH_{n-1}CO]^-$ (n = 6, 10, 12) are given in Table 2.

All the studied anions have significant HOMO–LUMO gaps (8–9 eV). All the anions except $[B_6H_5CO]^-$ have negative values of chemical potential μ. The values of chemical hardness η for corresponding monocarbonyl derivatives are in the range of 4.03–4.56 eV.

The strongest electrophile is $[B_{12}H_{11}CO]^-$, and the weakest one is $[B_6H_5CO]^-$. Based on the classification proposed by Domingo *et al.*[23,24] (electrophiles: $\omega > 1.50$ eV e strong, $1.50 > \omega > 0.80$ eV e moderate, $\omega < 0.80$ eV e marginal) the monocarbonyl derivatives of *closo*-borate anions can be attributed to marginal electrophiles. However, according to experimental data reported previously,[13] these anions have strong electrophilic character and can react under softs conditions with various nucleophiles such as water, alcohols, and amines. The reaction between $[B_{10}H_9CO]^-$ and H_2O is carried out in refluxing acetone and gives a high yield of the target product (75%). Thus, the proposed theoretical estimate[23,24] somewhat underestimates the electrophilic nature of *closo*-borate anions. Probably, it is not completely correct to directly compare the electrophilicity indices of boron clusters derivatives and such parameters for organic compounds (for which this classification was initially developed), and it is only reasonable to compare the carbonyl derivatives of boron clusters among themselves.

The active sites suitable for nucleophilic attack have been selected using the Fukui function indices based on the NBO and AIM atomic charges. In all cases, the most electrophilic site of all monocarbonyl derivatives of *closo*-borate anions is C-atom of the carbonyl group (Table 3). Anion $[B_{12}H_{11}CO]^-$ has maximum value of Fukui function on C-atom (0.48 for AIM and 0.46 for NBO), and anion $[B_6H_5CO]^-$ has minimum value of Fukui function on C-atom (0.36 for AIM and 0.34 for NBO).

Summarizing, we have carried out a systematic theoretical analysis of structure, bonding and reactivity of carbonyl derivatives of *closo*-borate anions $[B_nH_{n-1}CO]^-$ (n = 6, 10, 12), including electron density topological properties of main interatomic contacts, especially B–C interactions; reactivity descriptors for model systems calculated *via* DFT and the active sites suitable for nucleophilic attacks have been selected using the Fukui function indices based on the NBO and AIM atomic charges.

Table 3 Fukui functions of carbonyl group C-atom.

Anion	AIM based Fukui function	NBO based Fukui function
$[B_6H_5CO]^-$	0.36	0.34
$[1\text{-}B_{10}H_9CO]^-$	0.39	0.39
$[2\text{-}B_{10}H_9CO]^-$	0.43	0.40
$[B_{12}H_{11}CO]^-$	0.48	0.46

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.01.029.

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