Theoretical study of monocarbonyl derivatives of *closo*-borate anions [B*ₙ*H*ₙ₋₁*CO]⁻ (*n* = 6, 10, 12): bonding and reactivity analysis

Ilya N. Klyukin, Alexander S. Novikov, Andrey P. Zhdanov, Konstantin Yu. Zhizhin and Nikolay T. Kuznetsov

The full geometry optimization of all structures has been carried out at the ωB97X-D3/6-31++G(d,p) level of theory with the help of the ORCA 4.1.0 program package [S1]. 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. 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 (no imaginary frequencies). The topological analysis of the electron density distribution with the help of the quantum theory of atoms in molecules (QTAIM) formalism developed by Bader [S2] has been performed by using the Multiwfn program (version 3.6) [S3]. The electronic chemical potential μ, chemical hardness η and softness S, global electrophilicity ω have been calculated using the following formulas:

$$\mu = \frac{E_{HOMO} + E_{LUMO}}{2}$$

$$\eta = E_{LUMO} - E_{HOMO}$$

$$S = \frac{1}{\eta}$$

$$\omega = \frac{\mu^2}{2\eta}$$

The condensed Fukui functions (f_k^+) have been calculated on the basis of natural population analysis (NPA), and AIM charges using the following equations, where q_k(anion) and q_k(neutral) are the charges at atom k on the anion and neutral species, respectively:

$$f_k^+ = q_k(anion) - q_k(neutral)$$

We have estimated the B–C and C–O bond orders in the mono-carbonyl derivatives of closo-borate anions [BnHn-1CO]– (n = 6, 10, 12) using Wiberg bond order analysis (Table S1). The bond order of B-C bond is decreased with increasing of boron cluster size. Atomic charges.

Table S1 B–C and C–O Wiberg bond orders.

Anion	B–C bond order	C–O bond order
$[B_6H_5CO]^-$	1.22	2.58
$[1\text{-}B_{10}H_9CO]^-$	1.14	2.65
$[2\text{-}B_{10}H_9CO]^-$	1.07	2.68
$[B_{12}H_{11}CO]^-$	1.02	2.74

Main topological parameters of electron density for B–B and B–H interactions. These values of topological properties are close to those obtained for the corresponding $[B_nH_n]^{2-}$ anions [S4].

Table S2 Main topological parameters of electron density for B–B and B–H interactions.

	Bond length (Å)	$\rho(r)$ (e Å^{-3})	$\nabla^2\rho(r)$ (e Å^{-5})	H_b (h e^{-1})	ε	$\delta(A\text{-}B)$
B–B interactions	1.70–1.90	0.109 – 0.127	–0.087 – –0.196	–0.054 – –0.089	1.193 – 3.809	0.317 – 0.549
B–H interactions	1.19–1.21	0.161 – 0.171	–0.157 – –0,176	–0.167 – –0.175	0.000 – 0.070	0.689 – 0.706

$\rho(r)$ – Electron density at the bcp. $\nabla^2\rho(r)$ – Laplacian of electron density at the bcp. H_b – total energy at the bcp. ε – ellipticity at the bcp. $\delta(A–B)$ – delocalization index.

We have used QTAIM and NBO approaches for estimation of atomic charges. Firstly, we have considered atomic charges on B atoms bonded with *exo*-polyhedral substituent. The values of AIM charges are 0.02 ($[B_6H_5CO]^-$) – –0.34 ($[1\text{-}B_{10}H_9CO]^-$). The values of NBO charges are –0.41 ($[2\text{-}B_{10}H_9CO]^-$) – –0.52 ($[1\text{-}B_{10}H_9CO]^-$). Thus, the values of NBO charges of B atoms bonded with *exo*-polyhedral substituent are in a good agreement with previous reported data [S5]. The AIM charges on all another boron atoms are 0.46 – 0.71, and NBO charges are –0.16 – –0.52. The AIM charges of hydrogen atoms are –0.63 – – 0.68, and NBO charges are 0.00 – 0.06.

Also we have considered charges of carbon and oxygen atoms. Both approaches (AIM and NBO) have the same trend, but in case of NBO carbon atoms of carbonyl group have a more positive charges,

and oxygen atom have less negative charges than those in case of AIM. Anion $[B_{12}H_{11}CO]^-$ has maximum value of positive charge on C-atom (0.92 e for AIM and 0.93 e for NBO); anion $[B_6H_5CO]^-$ has minimum value of positive charge on C-atom (0.68 e for AIM and 0.86 e for NBO); anion $[B_6H_5CO]^-$ has maximum negative value of charge on oxygen (–1.25 e for AIM and –0.48 e for NBO); anion $[B_{12}H_{11}CO]^-$ has minimum value of negative charge on oxygen(–1.21 e for AIM and –0.40 e for NBO).

References

S1.   F. Neese, *WIREs Comput. Mol . Sci.*, 2012, **2**, 73.

S2.   R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, 1990.

S3.   T. Lu and F. Chen, *J. Comp. Chem.*, 2011, **33**, 580.

S4.   R. Bader and D. Legare, *Can. J. Chem.*, 1992, **70**, 657.

S5.   X.-F. Qin, H.-S. Wu and H. Jiao, *J. Mol. Struct. THEOCHEM*, 2007, **822**, 111.

Table S3. Cartesian atomic coordinates of the calculated equilibrium structures.

Compound	Atom	x	y	z
$[B_6H_5CO]^-$				
	B	−0.735969	9.553254	5.071085
	B	0.421787	9.854128	6.309541
	B	0.712021	10.483566	4.734320
	H	−1.9146730	9.7578940	4.979990
	H	0.9326750	11.5869180	4.3181160
	B	1.697800	9.1797060	5.3703440
	B	0.540461	8.875927	4.122265
	B	0.249866	8.249825	5.706850
	H	2.871025	9.022785	5.567426
	H	0.599661	8.386740	3.025626
	H	0.023835	7.194407	6.230704
	C	0.344534	10.440760	7.632003

	O	0.281275	10.908900	8.688016
[1-B$_{10}$H$_9$CO]$^-$				
	B	0.000182	1.652207	0.000031
	B	−0.499083	0.550471	−1.202701
	B	1.202793	0.550283	−0.499112
	B	0.499204	0.550362	1.202765
	B	−1.202673	0.550549	0.499175
	H	0.000309	2.847517	0.000031
	H	−0.929712	0.958416	−2.246041
	H	2.246177	0.958068	−0.929786
	H	0.929921	0.958216	2.246104
	H	−2.245968	0.958564	0.929848
	B	0.506611	−0.944144	−1.221056
	B	−0.000223	−2.005694	0.000032
	B	−1.221194	−0.943953	−0.506685
	B	−0.506824	−0.944031	1.221119
	B	1.220982	−0.944222	0.50675 0
	H	0.932506	−1.380121	−2.252855
	H	−2.253041	−1.379771	−0.932626
	H	−0.932813	−1.379917	2.252918
	H	2.252732	−1.380267	0.932694
	C	−0.000368	−3.461644	0.000035
	O	−0.000480	−4.610767	0.000036

[2-B$_{10}$H$_9$CO]$^-$				
	B	0.050074	1.950869	0.129486
	B	−0.449819	0.861664	−1.086883
	B	1.238147	0.827871	−0.441302
	B	0.510296	0.74205 0	1.235077
	B	−1.188793	0.820024	0.562243
	H	0.055676	3.144769	0.151858
	H	2.253326	1.255699	−0.910877
	H	0.944865	1.102342	2.29294 0
	H	−2.242604	1.242455	0.943378
	B	0.507581	−0.649272	−1.251792
	B	−0.045633	−1.79438 0	−0.126601
	B	−1.235751	−0.654387	−0.532844
	B	−0.519676	−0.747085	1.135751
	B	1.175216	−0.741854	0.436035
	H	0.92076 0	−0.95945 0	−2.334826
	H	−2.291839	−0.967369	−1.008862
	H	−0.966972	−1.182674	2.160322
	H	2.218955	−1.171668	0.842698
	H	−0.076958	−2.986554	−0.210582
	C	−0.937128	1.655317	−2.237938
	O	−1.302767	2.323639	−3.094446
[B$_{12}$H$_{11}$CO]$^-$				

	B	3.047793	6.571080	2.913813
	B	1.612357	5.501623	2.892860
	B	4.212694	5.943990	4.099519
	B	3.163023	7.308043	4.541331
	B	1.568487	7.039835	3.792001
	B	3.240541	4.811564	3.066571
	H	3.429154	7.140009	1.931415
	H	0.977536	5.311213	1.894854
	H	5.403532	6.010258	3.985317
	H	3.625912	8.399219	4.712163
	H	0.891970	7.957523	3.424072
	H	3.774930	4.111228	2.255164
	B	0.840776	5.577960	4.507271
	B	1.858023	4.190077	4.064544
	B	3.430135	6.021450	5.736090
	B	3.426709	4.526921	4.798150
	B	1.799191	6.694567	5.525881
	B	1.975464	4.936429	5.714620
	H	−0.340575	5.440588	4.652479
	H	1.458351	3.069658	3.926202
	H	4.092478	6.140265	6.727080
	H	1.297480	7.351362	6.392689
	H	1.656549	4.319588	6.690553

	C	4.275621	3.383703	5.259050
	O	4.923337	2.514179	5.610079
(CH₃)BH₂				
	B	−5.704296	1.748936	−0.013198
	C	−6.720315	0.561095	−0.036280
	H	−7.138023	0.459611	0.977352
	H	−6.206941	−0.391667	−0.217985
	H	−7.551959	0.662636	−0.737493
	H	−4.707944	1.664154	0.652888
	H	−5.888502	2.765314	−0.625274
(CH₃)₂BH				
	B	−5.814853	1.739724	0.298745
	C	−6.672735	0.512083	−0.169303
	H	−7.403866	0.321177	0.633393
	H	−6.107555	−0.413882	−0.315463
	H	−7.272243	0.721292	−1.061768
	H	−6.300841	2.840860	0.215997
	C	−4.357115	1.609154	0.864148
	H	−4.133221	2.322741	1.663916
	H	−4.077825	0.599273	1.181160
	H	−3.685055	1.880180	0.033014
(CH₃)₃B				
	B	−5.826584	1.769704	0.303855

	C	−6.680787	0.521954	−0.149255
	H	−7.083608	0.060196	0.765903
	H	−6.073619	−0.256655	−0.626100
	H	−7.535256	0.757103	−0.792056
	C	−4.383063	1.566909	0.910581
	H	−4.235556	2.163876	1.818707
	H	−4.111466	0.527477	1.120339
	H	−3.653706	1.959195	0.185678
	C	−6.421506	3.223308	0.135860
	H	−6.454595	3.457214	−0.938864
	H	−7.465658	3.269262	0.470328
	H	−5.857113	4.019397	0.631039
BH$_3$CO				
	B	−6.459973	2.920618	0.078482
	H	−5.558303	2.179972	0.396641
	H	−7.262744	3.129958	0.958667
	H	−6.956732	2.663916	−0.994076
	C	−5.775907	4.279830	−0.139137
	O	−5.271981	5.284506	−0.300576