Brief Communications

$[1\text{-}B_{10}H_9N_2]^-$ and $[1\text{-}CB_9H_{10}]^-$ anions: an attempt of quantum chemical calculations

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Comparative quantum chemical calculations of structural parameters, chemical shifts of ^{11}B NMR spectra, and atomic charges in 10-vertex boron hydride anions $[1\text{-}CB_9H_{10}]^-$ and $[1\text{-}B_{10}H_9N_2]^-$ were performed using the restricted Hartree—Fock method with the 6-31++G(D,P) basis set.

Key words: 10-vertex boron hydrides, 1-diazoniononahydro-*closo*-decaborate anion, 1-carba-*closo*-decaborate anion, ^{11}B NMR spectra, quantum chemical calculations.

The diazonium derivative of decahydro-*closo*-decaborate anion, $[1\text{-}B_{10}H_9N_2]^-$,[1,2] provides a unique example in chemistry of diazonium salts because of its high thermal[3] and chemical[2,4,5] stability due to strong electron-donor effect of the *closo*-decaborate polyhedron. At the same time it is interesting to study the reverse process, that is, the effect of the diazonium substituent on the properties of the boron polyhedron. Replacement of a hydrogen atom in the *closo*-decaborate anion by the diazonium group showing a strong electron-accepting effect should lead to significant deactivation of the boron framework. Unfortunately, the published data on the influence of the diazonium substituent on the reactivities of various BH groups in the $[1\text{-}B_{10}H_9N_2]^-$ anion are scarce.[2]

Recently,[6] in studies of proton—deuterium exchange in various derivatives of the *closo*-decaborate anion we found a successive reduction of the rate of the process in the order $[1\text{-}B_{10}H_9OR]^{2-} > [1\text{-}B_{10}H_9NR_3]^- \gg \gg [1\text{-}B_{10}H_9N_2]^-$; this confirms a strong deactivating effect of the $-N_2^+$ group. A similar effect was also observed when a boron atom in the polyhedron was formally replaced by a heteroatom, *e.g.*, a carbon atom. Quantitatively, the effect is characterized by the change in the chemical shift of the ^{11}B NMR spectra of the boron atom antipodal to the atom replaced.[7,8] Substitution of a carbon atom for a boron atom in the polyhedron affects the chemical shift of the antipodal atom much stronger than replacement of a hydrogen atom.[7]

* Dedicated to Academician G. A. Abakumov on the occasion of his 70th birthday.

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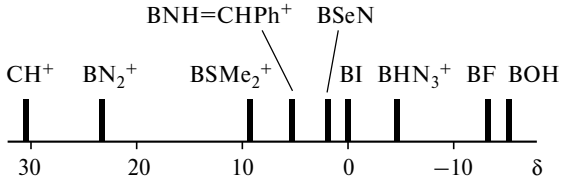

Fig. 1. ^{11}B NMR chemical shifts of B(10) atom in $[1\text{-}XB_9H_9]^{2-}$ anions (X = $BR^{0/+}$ or CH^+); $R^{+/0}$ = $^+N_2$, $^+SMe_2$, $H^+N{=}CHPh$, I, $^+NH_3$, F, OH.

Analysis of the ^{11}B NMR spectra of some derivatives of the *closo*-decaborate anion[4,5,9–13] revealed an unprecedentedly large, compared to the NMR spectra of other derivatives, low-field shift of the signal of the antipodal boron atom in the $[1\text{-}B_{10}H_9N_2]^-$ anion. The shift magnitude is similar to the chemical shift of the antipodal boron atom in 1-carba-*closo*-decaborate-anion $[1\text{-}CB_9H_{10}]^-$ [14] (Fig. 1). Therefore, it was of interest to carry out a comparative quantum chemical study of the $[1\text{-}B_{10}H_9N_2]^-$ and $[1\text{-}CB_9H_{10}]^-$ anions.

Geometry optimization of the 10-vertex *closo*-borate anions was performed by the restricted Hartree—Fock (RHF) method with the 6-31++G(d,p) basis set. The results obtained were compared with experimental X-ray analysis data for $(Et_3NH)[1\text{-}B_{10}H_9N_2]$[15] and $[Cp^*Ir(\mu\text{-}Cl)_3IrCp^*][1\text{-}CB_9H_{10}]$[16] and with the results of DFT B3LYP/6-31G(d),[17] RMP2(fc)/6-31G*,[18] and HF SCF/6-31+G* [19] calculations of the $[1\text{-}CB_9H_{10}]^-$ anion. The results of RHF/6-31++G(d,p) calculations of the $[1\text{-}CB_9H_{10}]^-$ anion agree with those obtained earlier using other quantum chemical methods. In addition, the calculations quite correctly reproduce the geometries of both anions under study.

The optimized geometric parameters were used in CSGT calculations of the ^{11}B NMR spectra. To compare the results of calculations and experimental data, signal assignment in the ^{11}B NMR spectra of $[1\text{-}CB_9H_{10}]^-$ and $[1\text{-}B_{10}H_9N_2]^-$ anions was done using ^{11}B—^{11}B COSY NMR spectroscopy (Fig. 2).

Comparison of the results obtained shows good correspondence between the calculated and experimental ^{11}B NMR chemical shifts for both anions (Fig. 3),

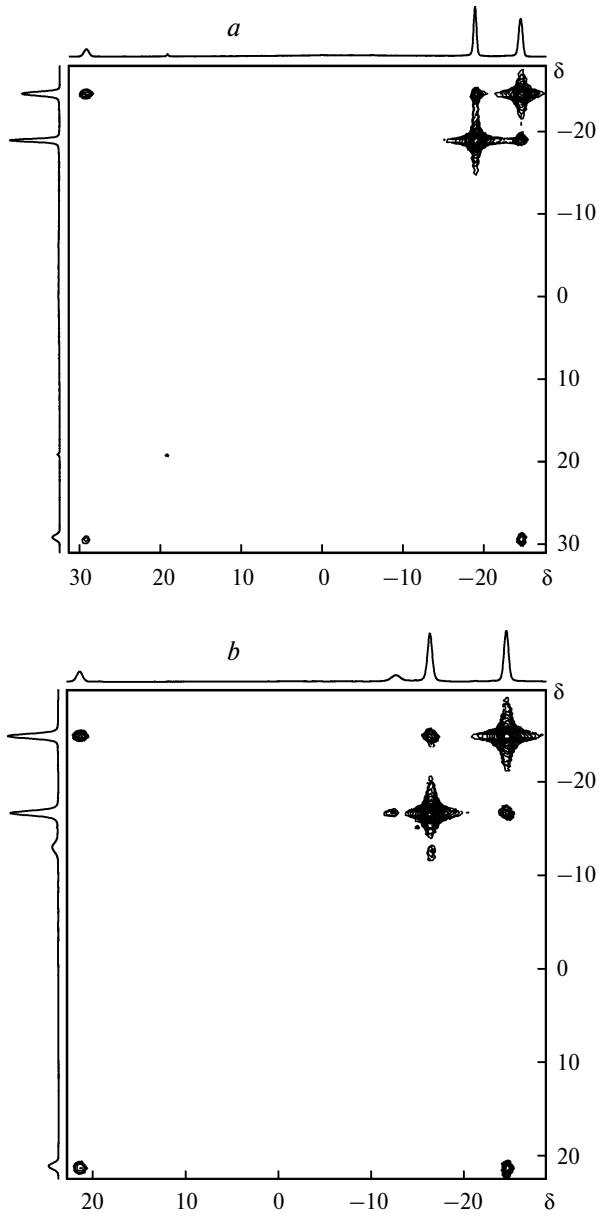

Fig. 2. ^{11}B—^{11}B COSY NMR spectra of anions $[1\text{-}CB_9H_{10}]^-$ (*a*) and $[1\text{-}B_{10}H_9N_2]^-$ (*b*).

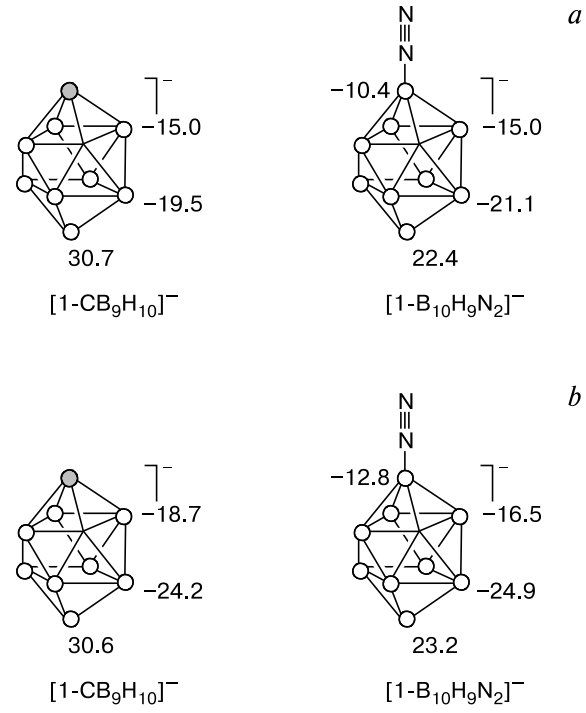

Fig. 3. Calculated (*a*) and experimental (*b*) ^{11}B NMR chemical shifts (δ) of $[1\text{-}CB_9H_{10}]^-$ and $[1\text{-}B_{10}H_9N_2]^-$ anions.

the CSGT-calculated chemical shifts for $[1\text{-}CB_9H_{10}]^-$ being similar to those obtained earlier from IGLO calculations.[8]

According to NBO calculations, the atomic charges in the polyhedra of these anions are as follows: –0.085 (B(2)—B(5)), –0.165 (B(6)—B(9)), and –0.180 (B(10)) for $[1\text{-}CB_9H_{10}]^-$ and –0.089 (B(2)—B(5)), –0.148 (B(6)—B(9)), and –0.196 (B(10)) for $[1\text{-}B_{10}H_9N_2]^-$. Despite a common pattern of the charge distribution in the both polyhedra the charges on the corresponding atoms in the systems under study are appreciably different. Probably, this can be explained by different contributions of the $—CH^+$ and $—BN_2^+$ groups to the delocalized electronic system of the boron cluster and by the stronger electron-accepting character of the CH group (total changes of the $—CH^+$ and $—BN_2^+$ fragments are –0.554 and +0.072, respectively).

It should be noted that the charges calculated in this work for the $[1\text{-}CB_9H_{10}]^-$ anion are similar to those obtained earlier by the DFT B3LYP/6-31+G(2d,p) [17] and MP2/6-31G(d,p) [20] methods.

A complex analysis of the results of theoretical studies including earlier ones and experimental data for the $[1\text{-}CB_9H_{10}]^-$ and $[1\text{-}B_{10}H_9N_2]^-$ anions suggests the following: 1) quantum chemical calculations quite correctly reproduce the molecular geometry and spectral characteristics of the 10-vertex *closo*-polyhedral boron hydrides; 2) calculated bond lengths are somewhat overestimated and the chemical shifts are underestimated compared to the corresponding experimental data; and 3) changes in the geometric parameters and spectral characteristics in both systems show some common features, but the calculated atomic charges in the polyhedra are considerably different, which indicates a stronger electron-accepting character of the $—CH^+$ group compared to the $—BN_2^+$ group. More detailed analysis of the substituent effect on the electronic structure of the 10-vertex boron hydrides requires additional comparative calculations of various *closo*-decaborate anion derivatives bearing substituents of different (electron-donor and electron-acceptor) nature.

Experimental

$Cs[1\text{-}CB_9H_{10}]$ and $(Et_3NH)[1\text{-}B_{10}H_9N_2]$ were synthesized following known procedures.[15,21] $^{11}B—^{11}B$ COSY NMR spectra were recorded on a Bruker AM-360 spectrometer. Geometry optimization of $[1\text{-}CB_{10}H_{10}]^-$ and $[1\text{-}B_{10}H_9N_2]^-$ anions with C_{4v} symmetry was carried out using the GAUSSIAN-98 program.[22] Geometric parameters of polyhedra were obtained from RHF/6-31++G(d,p) calculations. Atomic charges were calculated using the NBO model.

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